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# *A COMPARATIVE STUDY OF THE DIGESTION OF PROTEINS AND CARBOHYDRATES IN GOATS DURING INFUSORIA-FREE AND -INFECTED PERIODS*

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The purpose of the experiment was to determine the effect of the protozoa upon the digestion of proteins and carbohydrates in ruminants. The goat was chosen for the experimental animal because it seems to lend itself to laboratory conditions better than our other common ruminants. The experiment was planned so that a comparison of the results obtained in goats which had been rendered free of their rumen infusora for a definite period of time might be made with the results obtained for a like period after the animals were reinfected with the infusoria, which in our work were mostly members of the genus *Entodinium* and *Diplodinium*. The same amounts by weight of alfalfa hay and grain mixture were fed to any one goat during the infusoria-free period as during the period during which the goat carried the infusoria infection. Aliquot samples of the hay and grain which we fed to the animals were subjected to chemical analyses. By means of specially constructed crates all feces and urine from each goat were carefully collected. These materials were likewise subjected to chemical analyses. In all, four animals were conducted through digestion trials, and the digestibility coefficients of the protein, ether extract, nitrogen-free extract, crude fiber, hemicellulose, pentosans, alpha cellulose, and total dry matter were determined. The partition of nitrogen between feces and urine, as well as the amounts of nitrogen stored daily, were also calculated. The results are shown in the accompanying table.

An inspection of the above table will show that no significant advantage accrues to the host from the possession of the infusoria, so far as can be learned from the determinations made. This conclusion is quite contrary to beliefs expressed by certain protozoölogists and physiologists. The complete results of the experiment are now being written up for publication at a later date.

TABLE 1

SHOWING SUMMARY OF RESULTS

| GOAT NO. | PERIOD NO. | COEFFICIENTS OF DIGESTIBILITY | | | | | | | | EXCRETION OF NITROGEN | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PROTEIN | ETHER EXTRACT | NITROGEN FREE EXTRACT | CRUDE FIBRE | HEMI-CELLU-LOSE | PENTO-SANS | ALPHA CELLU-LOSE | TOTAL DRY MATTER | % TOTAL NITROGEN VOIDED IN FECES | % TOTAL NITROGEN VOIDED IN URINE | DAILY N. BAL. = GR. N. STORED DAILY | LENGTH OF PERIOD IN DAYS | AV. WT. OF GOAT DURING PERIOD IN LBS. | NET GAIN OR LOSS IN WT. DURING PERIOD IN LBS. |
| 1 | I | 68.07 | 68.78 | 74.81 | 35.32 | 44.42 | 48.74 | 45.25 | 62.08 | 40.32 | 59.68 | +1.79 | 14 | 37 | +3.0 |
| | II | 71.10 | 67.82 | 76.15 | 40.73 | 50.27 | 50.57 | 51.32 | 63.56 | 36.67 | 63.33 | +2.21 | 14 | 38 | 0 |
| 2 | I | 67.13 | 54.92 | 74.87 | 37.29 | 46.29 | 49.98 | 48.43 | 60.84 | 57.37 | 42.63 | +4.84 | 14 | 34.5 | +0.75 |
| | II | 68.78 | 52.94 | 76.58 | 38.17 | 48.49 | 49.92 | 49.99 | 62.03 | 46.35 | 53.65 | +3.70 | 14 | 36.25 | −2.0 |
| 3 | I | 67.36 | 56.58 | 76.40 | 39.16 | 48.48 | 51.79 | 52.55 | 61.61 | 35.36 | 64.64 | +0.93 | 21 | 59.25 | −2.25 |
| | II | 68.94 | 59.77 | 75.29 | 39.03 | 47.29 | 50.19 | 52.51 | 61.39 | 32.05 | 67.95 | +0.37 | 21 | 58 | +2.0 |
| 4 | I | 68.91 | 52.71 | 72.84 | 38.56 | 45.75 | 50.41 | 50.74 | 60.15 | 38.86 | 61.14 | +2.69 | 21 | 86 | +1.0 |
| | II | 71.09 | 63.62 | 76.41 | 34.95 | 45.98 | 49.97 | 48.91 | 61.84 | 36.58 | 63.42 | +2.82 | 21 | 83 | −1.0 |

I = infusoria-free period.
II = period of infection.

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## *THE MELANOPHORE ACTIVATOR OF THE EYE*

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The chromatic response of the skin to variation in background color depends mainly upon the presence of the eyes. In certain Crustacea (Koller, '28; Perkins, '28; Pouchet, '72) and in some reptiles and amphibians (Carlton, '03; Kropp, '27; Redfield, '18) the eyes are the chief organs of light reception and as such mediate most light stimuli that ultimately affect the chromatophores. The fact that a blinded animal may change color slightly when transferred from a light to a dark background does not alter the importance of the eyes, since in such cases the change from the expanded to the contracted condition, or in the reverse direction, is accomplished in twice the normal time and can be shown to be due to the presence of light receptors in the skin (Kropp, '27; Laurens, '15; Parker, '03). In most cases, when an animal is totally blinded, the chromatophores assume a state of extreme expansion or contraction and at most show only slight variations from this condition.

The nature of the rôle that the eyes play in normal "adaptive" color changes is a moot question. Conceivably, they may function (1) as organs that transmit directly along nervous paths stimuli that affect the chromatophores, or (2) as organs that affect the chromatophores reflexly by inducing the secretion of chromatophore activating substances of the endocrine glands. Perkins ('28) succeeded with Palaemonetes in obtaining the typical white-adapted condition in a blinded animal following the injection of a sea-water extract of eyes removed from white-adapted individuals. This was later confirmed by Koller ('28) on Crangon. It would seem, therefore, that there is produced in the eyes of these animals, under particular light conditions, a pigment-contracting substance which, carried in the blood stream, is responsible for the so-called white-adapted state.

In the course of some work on the pigmentary responses of frogs and

tadpoles, an attempt was made by blood transfusion methods to test the hypothesis that in normal color changes the blood carried a melanophore activating material. While this had been successfully done with Phrynosoma (Redfield, '18), my experiments were negative. Later, the eyes of dark-adapted tadpoles of Rana clamitans were removed and extracted in distilled water. The extract was prepared and injected in the absence of light. When light was used the results were indifferent or negative. Such extracts were injected in small quantity into the abdominal cavities of normal light-adapted tadpoles and it was found that animals so treated showed the melanophore expanded state characteristic of dark-adapted tadpoles. This change occurred in from 5 to 30 minutes and lasted for 2 to 3 hours regardless of light and background conditions. Four eyes were macerated quickly and thoroughly in 1 cc. of distilled water, filtered rapidly and 0.1 cc. to 0.2 cc. of the clear filtrate injected into the abdominal cavity. Controls were injected with an equivalent amount of distilled water.

The reverse experiment, namely, the injection of extracts from the eyes of light-adapted animals into normal dark-adapted ones, has thus far yielded no clear-cut results. Nor has it been possible to obtain similar reactions in the case of adult frogs. However, with the minnow, *Fundulus*, the results have paralleled those with the tadpole and been even more satisfactory. Neither sea-water nor Ringer's solution was of service as an extraction medium since they apparently destroyed in part the active material. Furthermore, the use of these fluids tends to complicate matters since each causes melanophore contraction when injected alone.

The origin and nature of this melanophore activating agent cannot be stated with certainty. Preliminary work shows that the probable source is in the retina, since the reaction can be obtained when lens, cornea and iris are eliminated and the posterior half of the eye-ball alone extracted.

Carlton, F. C., *Proc. Amer. Acad. Arts and Sci.*, **39**, 257–276, 1903.
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Kropp, B., *J. Exp. Zoöl.*, **49**, 289–318 (1927).
Laurens, H., *Ibid.*, **18**, 577–638, 1915.
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## NOTE ON MR. KING'S PAPER: "THE CRYSTAL STRUCTURE OF STRONTIUM"

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In No. 4 of this periodical King stated that on redetermining the crystal structure of strontium he found a cubic face-centered lattice in agreement with our measurements,[1] but that the unit cubic edge ($a_0 = 6.075 \pm 0.004$ A.U.) was 0.7% greater than ours, which figured 6.03 A.U. King believes that this rather considerable discrepancy is due to the fact that his measurements, which were carried out with a view to obtaining very accurate results, were more exact than ours. We feel bound to point out that this is not the reason, but that our spacing applies to liquid air temperature—a fact that King has apparently overlooked—whereas his value holds for room temperature. The difference in question cannot be calculated accurately but can be gauged at 0.03 A.U. $\pm$ 10% by the usual approximation as shown in our paper. Computed for room temperature our result would thus be 6.06 A.U. The difference between this value and King's is within the limits of our experimental error. We will not discuss the question whether our value or King's is the more accurate, but we may mention that in a recent paper Ebert[2] gives the unit cubic edge of strontium as 6.05 A.U. at room temperature.

[1] *Zeit. phys. Chemie*, **133**, 165, 1928.

[2] *Zeit. anorg. Chemie*, **179**, 4, 1929.

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## THE RAMAN SPECTRUM OF GYPSUM

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In an investigation of the Raman spectra of some ionized substances in aqueous solution, it was found[1] that the frequency shift given by a solution of potassium carbonate was in fairly close agreement with the strongest shift given by calcite. Data for such a comparison in other cases do not appear to exist, for change of frequency on scattering has been measured for only a few crystalline substances. In addition to calcite,[2,3,5] these are quartz,[2,3,4,6] ice,[5] and topaz.[6] No modified frequencies were found in the light scattered by halite,[2] NaCl, fluorite,[5]

$CaF_2$, or by the salts[7] LiF and NaF. In the present paper are described the results of measurements on gypsum, $CaSO_4.2H_2O$, and a comparison of these with data on ammonium sulfate solution.

The crystal used was a clear, colorless specimen internally free from cleavage cracks. It was about 15 cm. long and had a cross-section of about 2 $cm.^2$; the long edges of the prism faces were parallel to the *c*-axis. The crystal was placed in a water-jacketed glass tube with an end window and irradiated with light from a mercury arc. The arc was placed parallel

TABLE 1

RAMAN SPECTRA FROM GYPSUM

| FREQUENCY OF SHIFTED LINE, $CM.^{-1}$ | INTENSITY OF SHIFTED LINE | WAVE LENGTH OF EXCITING LINE, Å | FREQUENCY OF EXCITING LINE, $CM.^{-1}$ | FREQUENCY CHANGE, $CM.^{-1}$ |
|---|---|---|---|---|
| 24291.5 | Weak | 4046.56 | 24705.5 | 414.0 |
| 24085.0 | Very weak (broad) | 4046.56 | 24705.5 | 620.5 |
| 24033.6 | Very weak | 4046.56 | 24705.5 | 671.9 |
| 23985.7 | Medium (broad) | 3650.15 | 27388.4 | 3402.7 |
| 23949.3 | Weak (broad) | 3654.83 | 27353.3 | 3404.0 |
| 23896.1 | Strong (very broad) | 3650.15 | 27388.4 | 3492.3 |
| | | (3663.27) | (27290.5) | (3394.4) |
| 23861.4 | Medium weak (broad) | 3654.83 | 27353.3 | 3491.9 |
| 23798.1 | Medium weak (broad) | 3663.27 | 27290.5 | 3492.4 |
| 23697.8 | Strong | 4046.56 | 24705.5 | 1007.7 |
| 23569.3 | Medium | 4046.56 | 24705.5 | 1136.2 |
| 23507.2 | Very weak | 4077.8 | 24516.1 | 1008.9 |
| 23351.5 | Very faint | 4358.34 | 22938.1 | −413.4 |
| 22523.0 | Medium weak | 4358.34 | 22938.1 | 415.1 |
| 22445.2 | Very weak | 4358.34 | 22938.1 | 492.9 |
| 22318.6 | Weak (broad) | 4358.34 | 22938.1 | 619.5 |
| 22267.3 | Weak | 4358.34 | 22938.1 | 670.8 |
| 21987.1 | Very weak | 4347.50 | 22995.3 | 1008.2 |
| 21929.9 | Very strong | 4358.34 | 22938.1 | 1008.2 |
| 21803.3 | Medium strong | 4358.34 | 22938.1 | 1134.8 |
| 21303.2 | Medium strong (broad) | 4046.56 | 24705.5 | 3402.3 |
| 21215.2 | Strong (broad) | 4046.56 | 24705.5 | 3490.3 |

to the *c*-axis of the crystal, and scattered light from the crystal was taken off in the direction of the *c*-axis. Since the end of the crystal was quite irregular, the crystal was submerged in chlorobenzene which has a refractive index close to those of gypsum. To insure that no scattered lines had reached the spectrograph from the liquid, carbon tetrachloride, which gives a quite different Raman spectrum from chlorobenzene, was used in one case with no change in the observed scattered lines. The glass tube containing the crystal was painted black around the ends of the crystal. The light from the crystal was converged with lenses and thrown on the spectrograph slit with the aid of a reflecting prism.

The spectrograph was a two-prism glass instrument arranged with interchangeable camera lenses so as to give either a dispersion of about

100 cm.$^{-1}$ per mm. with an aperture of f 8, or a smaller dispersion and higher speed corresponding to an aperture of f 3. A comparison spectrum of the iron arc was recorded on each plate, and the plates measured on a Gaertner comparator. The frequencies of the shifted lines were computed by linear interpolation between the frequencies of closely neighboring iron lines.

The measured frequencies and estimated intensities of the modified lines are given in the first two columns of table 1. The wave-lengths and frequencies of the corresponding exciting lines are given in the third and fourth columns, respectively, while the frequency shifts are given in the last column. As a control on the assignment of exciting lines to the various observed lines, we have made a photograph while flowing through the water-jacket an alkaline solution of potassium chromate of a concentration such that considerable light of wave-length λ 4358 was trans-

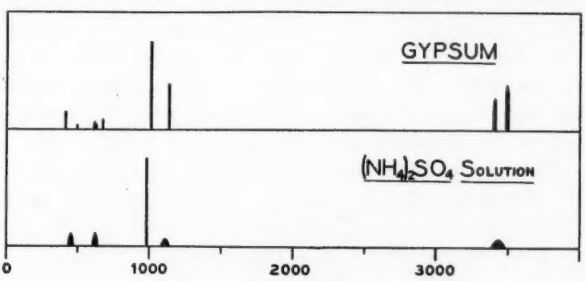


FIGURE 1

mitted, while that of shorter wave-length was largely absorbed. All of the modified lines appearing on this photograph were ones for which excitation by λ4358 is indicated in table 1, and all lines thus indicated appeared on the photograph with the exception of the very faint anti-Stokes line.

The data of table 1 indicate eight different frequency shifts; the best values of these are summarized in table 2.

TABLE 2

FREQUENCY SHIFTS GIVEN BY GYPSUM

| Frequency shift (cm.$^{-1}$) | 414.2 | 492.9 | 620.0 | 670.4 | 1008.2 | 1135.5 | 3403.0 | 3491.5 |
|---|---|---|---|---|---|---|---|---|
| Intensity | Med. weak | Very weak | Weak (broad) | Weak | Very strong | Med. strong | Med. strong (broad) | Strong (broad) |

We have also rephotographed the spectrum from ammonium sulfate solution using higher dispersion than previously.[1] The new measurements yield the following values for the frequency shifts of the Raman lines pre-

viously reported: 451, medium (broad); 620, medium (broad); 980.3, strong. In addition there appears to be a very broad shift with $\Delta\nu \cong 1113$ as well as the still broader band due to water with $\Delta\nu$ equal to about 3430. With this higher dispersion it is especially evident that the strongest line is far sharper than the others. A comparison of this spectrum with that of gypsum is shown in figure 1.

The two largest frequency shifts given by gypsum are presumably due to water of crystallization while the smaller shifts are very likely due to sulfate ion. Schaefer and Schubert[8] measured residual rays from a variety of sulfates and concluded that all sulfates possess prominent maxima of reflection in the neighborhood of 9 and 16$\mu$ which are to be attributed to the sulfate ion. In the case of gypsum, the maxima occurred at 8.74 and 14.84$\mu$ with a weak maximum at 8.62$\mu$, and another weak one at about 3$\mu$ due to water of crystallization. The two prominent maxima correspond to frequencies of 1143 and 674 cm.$^{-1}$, respectively, in reasonable agreement[9] with the values 1135.5 and 670.4 which we have found. The two smallest Raman shifts do not fall in the range of the residual ray measurements. The absence of any maximum corresponding to the strongest Raman line ($\Delta\nu = 1008.2$) suggests that the initial and final states of the transition producing it are without electric moment, as Carelli, Pringsheim and Rosen[10] have suggested for an analogous line in the case of calcite. This appears to afford a reasonable explanation of the sharpness of this line in aqueous sulfate solution; for absence of electric moment would presumably minimize the interaction between sulfate ion and water molecules.

If the symmetry of the sulfate ion in aqueous solution may be taken as tetrahedral, Brester's[11] considerations concerning the multiplication of characteristic frequencies consequent upon removal of symmetry afford one possible explanation of the multiplicity of lines found from gypsum. The point group symmetry of this crystal is monoclinic holohedral. The space groups symmetry has been reported by Onorato[12] to be $C_{2h}^3$ with $8CaSO_4.2H_2O$ in a unit of structure that employs a face-centered lattice; if an end-centered lattice is used, the number of $CaSO_4.2H_2O$ becomes four. If the sulfur atoms occupy equivalent positions, the sulfate ion can, strictly speaking, have only either a center of symmetry, a two-fold axis, or a plane of symmetry in this crystal although it may approximate to a higher symmetry. If the sulfur atoms are not all in equivalent positions, a multiplication of lines could result for this reason. In any case, it is also possible that the weaker Raman lines do not represent fundamental frequencies.

[1] Dickinson and Dillon, *Proc. Nat. Acad. Sci.*, **15**, 334 (1929).

[2] R. W. Wood, *Phil. Mag.*, **6**, 729 (1928).

[3] Gr. Landsberg and L. Mandelstam, *Zeit. Phys.*, **50**, 769 (1928).

[4] P. Pringsheim and B. Rosen, *Zeit. Phys.*, **50**, 741 (1928).
[5] I. R. Rao, *Indian J. Physics*, **3**, 123 (1928).
[6] H. Nisi, *Proc. Imp. Acad. of Japan*, **5**, 127 (1929).
[7] C. Schaefer, *Zeit. Phys.*, **54**, 153 (1929).
[8] Schaefer and Schubert, *Ann. Phys.*, **50**, 283 (1916).
[9] This agreement may be fortuitous because of the fact that maxima of reflection and absorption are not quite coincident and are sometimes very appreciably removed from each other. See, for example, Havelock, *Proc. Roy. Soc.* **105A**, 488 (1924).
[10] Carelli, Pringsheim and Rosen, *Zeit. Phys.*, **51**, 511 (1928).
[11] Brester, *Ibid.*, **24**, 324 (1924).
[12] E. Onorato, *Zeit. Krist.*, **66**, 504 (1928).

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## *RAMAN SPECTRA FROM ACETONE*

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Measurements of Raman spectra from acetone have been published in a recent paper.[1] These measurements were so interpreted that out of thirteen modified lines, twelve corresponded to frequencies of observed infra-red absorptions, the thirteenth lying outside the range of the infra-red measurements. This result is surprising; for the occurrence of frequency shifts in Raman effect without the appearance of the corresponding infra-red absorptions is a very common phenomenon. We have examined Raman spectra from acetone; and as both our measurements and our interpretation disagree with those mentioned above, it seems desirable to report them.

The acetone used was Merck's "C.P." It was distilled through a 30 cm.-Eastman fractionating column the product used all coming over within 0.05° of 55.7° at 746 mm. It is important to use materials of reasonable purity; we have, for example, found it possible to bring out the strongest benzene lines from a carbon tetrachloride solution containing only 0.46% benzene.

The acetone was irradiated with light from a glass mercury arc, and the spectra photographed with a glass spectrograph having a dispersion of about 100 cm.$^{-1}$ per mm. in the blue. The iron arc was used as a standard.

The measured frequencies of the shifted lines together with their intensities are given in the second and third columns of table 1. Comparison of these measurements with those which have already been reported[1] shows considerable disagreement even among the strongest lines. Apparently seven lines are concerned in the production of these Raman lines. The wave-lengths and frequencies of these mercury lines are:

| | | | |
|---|---|---|---|
| I | 3650.15 Å 27388.4 cm.$^{-1}$ | V | 4077.8 Å 24516.1 cm.$^{-1}$ |
| II | 3654.83 Å 27353.3 cm.$^{-1}$ | VI | 4347.50 Å 22995.3 cm.$^{-1}$ |
| III | 3663.27 Å 27290.5 cm.$^{-1}$ | VII | 4358.34 Å 22938.1 cm.$^{-1}$ |
| IV | 4046.56 Å 24705.5 cm.$^{-1}$ | | |

TABLE 1

OBSERVED RAMAN LINES FROM ACETONE

| NO. | OBSERVED FREQUENCY OF SHIFTED LINE, CM.$^{-1}$ | ESTIMATED INTENSITY OF SHIFTED LINE | ASSUMED ORIGIN OF LINE | CALCULATED FREQUENCY OF SHIFTED LINE, CM.$^{-1}$ |
|---|---|---|---|---|
| 1 | 24464.4 | Very strong | I − *m* | 24464.6 |
| 2 | 24428.1 | Strong | I − *n* | 24421.8 |
| | | | II − *m* | 24429.5 |
| 3 | 24383.5 | Medium | I − *o* | 24382.0 |
| | | | II − *n* | 24386.7 |
| 4 | 24367.5 | Strong | III − *m* | 24366.7 |
| | | | II − *o* | 24346.9 |
| 5 | 24316.1 | Weak | III − *n* | 24323.9 |
| | | | IV − *a* | 24314.0 |
| 6 | 24284.7 | Weak | III − *o* | 24284.1 |
| 7 | 24212.9 | Very weak | IV − *b* | 24213.5 |
| 8 | 24174.0 | Medium weak | IV − *c* | 24175.5 |
| 9 | 23918.3 | Strong | IV − *d* | 23917.5 |
| 10 | 23727.1 | Medium weak | V − *d* | 23728.1 |
| 11 | 23639.0 | Medium weak | IV − *g* | 23638.1 |
| 12 | 23482.7 | Medium | IV − *h* | 23482.7 |
| 13 | 23366.5 | Very weak | IV − *i* | (23366.5) |
| 14 | 23275.5 | Medium (broad) | IV − *j* | 23275.0 |
| 15 | 22546.6 | Medium | VII − *a* | (22546.6) |
| 16 | 22446.7 | Weak | VII − *b* | 22446.1 |
| 17 | 22407.6 | Medium | VII − *c* | 22408.1 |
| 18 | 22207.0 | Very weak | VI − *d* | 22207.3 |
| 19 | 22150.9 | Very strong | VII − *d* | 22150.1 |
| 20 | 22032.5 | Very weak | VII − *e* | (22032.5) |
| 21 | 22009.7 | Very weak | VII − *f* | (22009.7) |
| 22 | 21869.8 | Medium | VII − *g* | 21870.7 |
| 23 | 21782.5 | Very strong | IV − *m* | 21781.7 |
| 24 | 21738.9 | Medium strong | IV − *n* | 21738.9 |
| 25 | 21712.0 | Medium strong | VII − *h* | 21715.3 |
| 26 | 21696.2 | Medium strong | IV − *o* | 21699.1 |
| 27 | 21590.0 | Medium strong | V − *m* | 21592.3 |
| | | | VII − *i* | 21599.1 |
| 28 | 21507.2 | Medium strong (broad) | VII − *j* | 21507.6 |
| 29 | 21227.1 | Strong | VII − *k* | (21227.1) |
| 30 | 21190.1 | Very weak | VII − *l* | (21190.1) |
| 31 | 20069.9 | Very weak | VI − *m* | 20071.5 |
| 32 | 20015.5 | Strong | VII − *m* | 20014.3 |
| 33 | 19972.4 | Medium weak | VII − *n* | 19971.5 |
| 34 | 19931.7 | Medium weak | VII − *o* | 19931.7 |

The strongest of these lines are I, IV and VII. Lines V and VI are so weak as to be involved in the production of only the most prominent Raman shifts. The modified lines are all accounted for by using the frequency differences summarized in table 2.

TABLE 2

FREQUENCY SHIFTS FROM ACETONE

| DESIGNATION OF SHIFT | FREQUENCY SHIFT, CM.$^{-1}$ | RELATIVE INTENSITY OF SCATTERING | $\lambda$ RAMAN $\mu$ | $\lambda$ I. R. $\mu$ | RELATIVE INTENSITY OF ABSORPTION |
|---|---|---|---|---|---|
| *a* | 391.5 | Medium | (25.6) | | |
| *b* | 492.0 | Weak | (20.3) | | |
| *c* | 530.0 | Medium | (18.9) | | |
| | | | | 13.10 | 2.3 |
| *d* | 788.0 | Very strong | 12.69 | 12.63 | 2.2 |
| *e* | 905.6 (?) | Very weak | 11.03 | 11.30 | 1.2 |
| *f* | 928.4 (?) | Very weak | 10.77 | 10.90 | 4.0 |
| | | | | 10.40 | 0.2 |
| | | | | 9.70 | 0.2 |
| *g* | 1067.4 | Medium | 9.38 | 9.10 | 2.0 |
| *h* | 1222.8 | Medium strong | 8.17 | 8.30 | 4.0 |
| *i* | 1339.0 (?) | Very weak | 7.47 | 7.60 | 0.3 |
| | | | | 7.30 | 0.5 |
| *j* | 1430.5 | Medium (broad) | 6.99 | 6.98 | 0.4 |
| | | | | 6.60 | 0.5 |
| *k* | 1711.0 | Strong | 5.84 | | |
| *l* | 1748.0 (?) | Very weak | 5.72 | 5.75 | 5.2 |
| | | | | 4.70 | 1.5 |
| *m* | 2923.8 | Very strong | 3.42 | 3.41 | 4.0 |
| *n* | 2966.6 | Strong | 3.37 | | |
| *o* | 3006.4 | Strong | 3.27 | | |

In the fifth column of table 1 are given calculated frequencies of modified lines obtained assuming the various lines to originate in the way indicated in the fourth column. (For example, I—*m* is the mercury line I of frequency 27388.4 cm.$^{-1}$ shifted by the amount 2923.8 cm.$^{-1}$ which is shift *m*.) It may be seen that the assumed origins of the lines are such that modified lines corresponding to any one shift have qualitatively (allowing for the smaller sensitivity of the plate toward the green) the same relative intensities as the mercury lines producing them. Several of the lines in table 1 (Nos. 2, 3, 4, 5 and 27) should result from the approximate superposition of two or more modified lines; measurements of these have been disregarded in selecting the best values given in table 2.

The fairly strong shift *k* ($\Delta\nu$ = 1711.0) occurs only once (line 29); Hg 4046 shifted by this amount would produce a line almost coincident with Hg 4347. If, however, a different origin were assumed for line 29 we should expect to find other lines not occurring on the plate. To account for lines 13, 15, 20, 21 and 30 corresponding to shifts *i*, *a*, *e*, *f* and

*l* we have also found it necessary to assume five frequency shifts not otherwise employed. When a potassium chromate filter was used, line 15 was greatly strengthened compared with, for example, lines 12 and 14; this leaves little doubt that line 15 arises from Hg 4358 modified by shift *a*. There remains, possibly, some ambiguity in the origin of lines *e*, *f*, *i* and *l*. We have attempted to remove this ambiguity by using the potassium chromate filter; but because of the extreme weakness of these lines we have not been entirely successful.

In the fourth column of table 2 are given calculated infra-red wavelengths corresponding to the frequency shifts. In the fifth and sixth columns are the wave-lengths and intensities of the maxima of infra-red absorption observed by Coblentz.[2] If a latitude of 0.3$\mu$ be allowed, all of the observed Raman shifts can be brought into agreement with infra-red absorption maxima in so far as the investigated regions overlap. In view of the considerable number of frequencies involved in both spectra, the necessity of allowing so much latitude leaves some of the coincidences unconvincing. In any case, the intensities in scattering and in absorption bear no evident relation. This question has been discussed elsewhere.[3]

[1] J. W. Williams and A. Hollaender, *Proc. Nat. Acad. Sci.*, **15**, 421 (1929).
[2] Coblentz, "Investigation of Infra-red Spectra," *Carnegie Inst. Publications*, **1** (1905).
[3] Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34** (1929).

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## *THE THERMAL DECOMPOSITION OF ACETONE IN THE GASEOUS STATE*

BY F. O. RICE AND R. E. VOLLRATH*

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Communicated August 2, 1929

In the field of reaction kinetics, the study of unimolecular homogeneous gas reactions is, from a theoretical standpoint, most interesting. At the present time but few really homogeneous, unimolecular reactions are known and this work was undertaken with the object of extending the number of organic decompositions of this type. In all the investigations of such decompositions made so far, the method used to follow the reaction has been to measure the rate of increase of pressure and from this to obtain the velocity constant. This method has two obvious disadvantages: (1) we must know what the products of decomposition are, and (2) these must not decompose or react with each other appreciably at the temperature of the experiment. Unfortunately in the case of organic compounds, these conditions seriously limit experimental work so that the decomposi-

tion of an organic series cannot be followed using this method. Consequently we have developed a method in which we follow the concentration of the decomposing compound analytically and in this way avoid all the troublesome uncertainties connected with the products of decompositions; provided that these do not react with the decomposing substance, and that we are dealing with a single homogeneous unimolecular change, our measurement of the rate should be free from error. The limitation of this method is that we must devise a quantitative method for estimating the organic compound; fortunately this can be done in a great many classes of compounds so that this method enables us greatly to extend the range of these investigations.

1. *Previous Work.*—Hinshelwood and Hutchinson[1] have recently measured by a manometric method, the rate of decomposition of acetone vapor in a quartz bulb maintained at temperatures of 500–600°C. They deduced from their results that the decomposition is unimolecular and in accordance with the following scheme:

$$CH_3COCH_3 \longrightarrow CO + CH_3 + CH_3.$$

The two methyl groups then react to give methane, ethylene and hydrogen.

It is well known[2], however, that when acetone is passed through a heated glass tube, methane separates from the molecule and ketene results, according to the following equation,

$$CH_3COCH_3 \longrightarrow CH_2{:}CO + CH_4$$

and Taylor[3] has suggested the possibility that Hinshelwood and Hutchinson really measured the rate of thermal decomposition of ketene. Apart from any uncertainty in the previous work it seemed desirable to develop a method which would be applicable not only to acetone but to its homologs, since a knowledge of their rates of decomposition and energies of activation would be of great interest.

2. *Experimental Method.*—A flow system was employed in which pure dry nitrogen saturated with the vapor of the acetone or higher ketone was passed at a known rate through a quartz tube heated in an electric furnace. The gases were then passed into a series of small wash bottles containing water in which the acetone could be estimated by hydroxylamine hydrochloride,[4] or by Messinger's method.[5] This method had been already worked out in this Laboratory;[6] in order to prove that the products of the decomposition did not react with the acetone it seemed desirable to show that one molecule of CO was present for every molecule of acetone decomposed. Dr. Slagle[6] had shown that the quantity of CO produced was much less than that expected. Consequently we tested for the presence of ketene in the gases leaving the tube and found very

considerable quantities. We therefore made measurements of the amounts of ketene formed when acetone is heated in a quartz tube.

3. *Experimental Results.*—A preliminary experiment confirmed the presence of ketene in the gases coming from the quartz tube at 630°C.; these were passed through a solution of aniline in ether and the excess aniline and ether was evaporated off. The residue was shown to be acetanilide by the melting point and by mixing the residue with acetanilide and taking a second melting point. In this preliminary experiment about 20% of the acetone introduced into the quartz tube was converted into ketene. The amount of ketene was also determined by absorbing it in $N/10$ sodium hydroxide and measuring the amount of base neutralized. Using this method, a number of runs were made to determine the influence of rate of flow on the yield of ketene and the results are summarized in table 1. An additional series of experiments was then performed to find

TABLE 1

TEMPERATURE OF FURNACE = 635°C.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Min. in furnace | 1.56 | 1.56 | 2.36 | 2.36 | 4.00 | 4.00 | 4.00 |
| Mols ketene formed per mol. acetone introduced | 0.256 | 0.260 | 0.255 | 0.254 | 0.249 | 0.254 | 0.249 |

what proportion of the decomposed acetone could be recovered as ketene and the results are given in table 2. The average half-life for acetone at

TABLE 2

TEMPERATURE OF FURNACE = 588°C.

| | | | | |
|---|---|---|---|---|
| Acetone introduced (gram) | 0.4135 | 0.4213 | 0.3357 | 0.4008 |
| Acetone undecomposed (gram) | 0.3522 | 0.3624 | 0.2711 | 0.3499 |
| Acetone decomposed (gram) | 0.0613 | 0.0589 | 0.0646 | 0.0509 |
| Mols ketene formed per mol. acetone (decomposed) | 0.559 | 0.582 | 0.552 | 0.622 |
| Time in furnace (min.) | 2.42 | 2.45 | 2.47 | 2.42 |

this temperature is 2.5 min. as compared with 3.1 min. obtained by Hinshelwood and Hutchinson.[1]

4. *Discussion.*—The results obtained so far show that for every 100 molecules of acetone decomposed approximately 60 molecules of ketene can be recovered, which is about the same as the yields reported by Hurd and Tallyn[7] who heated the acetone in a pyrex tube. It seems likely, therefore, that the primary process in the homogeneous unimolecular decomposition of acetone is the separation of a molecule of methane and formation of ketene. Presumably at the high temperature in the furnace the ketene undergoes a bimolecular decomposition as follows:

$$2CH_2{:}CO = C_2H_4 + 2CO.$$

According to this scheme 100 molecules of decomposed acetone should give 100 molecules of methane, 30 molecules of ethylene and 60 molecules

of carbon monoxide, which corresponds very closely with the results of the gas analysis made by Hinshelwood and Hutchinson.[1]

5. *Conclusion.*—The decomposition of acetone has been followed by an analytical method and it has been found that about 60% of the acetone decomposed can be recovered as ketene. Methods in which rate of change of pressure are used for following the course of the reaction are therefore unreliable.

* DU PONT FELLOW.

[1] Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, **111A**, 245 (1926).

[2] See Hurd, *The Pyrolysis of Carbon Compounds*, p. 247. Chemical Catalog Co., **1929.**

[3] Taylor, *J. Phys. Chem.*, **30**, 1433 (1926); book review.

[4] Meyer, *Lehrbuch der Organisch-Chemischen Methodik*, p. 846. Springer, **1922.**

[5] Goodwin, *J. Am. Chem. Soc.*, **42**, 39 (1920).

[6] Slagle, Dissertation, "Decomposition of Aliphatic Ketones in the Gas Phase," Johns Hopkins University, **1929.**

[7] Hurd and Tallyn, *J. Am. Chem. Soc.*, **47**, 1427 (1925).

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## *THE EQUILIBRIUM CONSTANTS OF REACTIONS INVOLVING HYDROXYL*

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A recent interpolation of band spectra data has indicated that the heat of dissociation of OH should be 138 k. cal.[1] An accurate value for the heat required in this dissociation would enable one to calculate the equilibrium constants of reactions involving this molecule.[2] Thus Bonhoeffer[3] and Reichardt have calculated the equilibrium constant of the following reaction, using their value for the heat of dissociation of water into H and OH:

$$2H_2O = H_2 + 2OH \qquad K_{OH} = \frac{[H_2]\,[OH]^2}{[H_2O]^2}$$

As my value for the heat of dissociation of OH is some 14 k. cal. larger than that corresponding to Bonhoeffer and Reichardt's data, I have recalculated their constants and contributed some additional ones.

In order to calculate the free energies of these reactions, use was made of the familiar equations:

$$F = H - TS$$

$$\Delta F = \Delta H - T\Delta S = -RT \ln K$$

$$\Delta H = D_0 + \sum_i \nu_i \left( \frac{5}{2} RT + E_{rot.\ +\ vibr.\ +,\ etc.} \right)$$

$$\frac{\Delta F}{T} = + \frac{D_0}{T} - \Delta S',$$

where

$-D_0 = Q_0$ = heat of reaction at absolute zero and

$$S = S' + \frac{5R}{2} + \frac{E}{T}.$$

The entropies were obtained from an application of the method of Gibson and Heitler.[4] In these methods involving the statistical interpretation of the third law of thermodynamics, the entropy of the molecule is considered to be the sum of its translational entropy,

$$S_t = R \ln \frac{(2\pi mkt)^{3/2} V}{h^3 \quad N} e^{5/2}$$

its rotational entropy, its vibrational entropy, and that due to all its different possible kinds of orientation. The latter may be expressed[5] in short by

$$S_m = \frac{E_m}{T} + R \ln \sum_n p_n e^{-\epsilon n/kT},$$

where $p_n$ is the *a priori* probability of the state $n$. This applies equally well to entropy of vibration and rotation, and, in these cases, $E_m$ is the total amount of the corresponding energy, i.e., $E_{vibration}$ $E_{rotation}$ $E_{orientation}$ (= 0 for a degenerate state).

As a further check on the reliability of this method, beyond that already shown by Gibson and Heitler, the entropies of oxygen and hydrogen at 25°C. were calculated. The count of the rotational entropy is simplified in the case of oxygen because there is only one kind present (symmetric or antisymmetric), as is shown by the fact that its band spectrum consists of alternately missing lines. Its theoretical entropy comes out to be 50.7, whereas the thermal values range from 45.6 to 49.2.[6] This high value comes from the inclusion of the $^3S$ spectroscopic state of the oxygen molecule.[7] If it were not for its triplet character, the calculated entropy would be 48.5. If the discrepancy is not due to calorimetric errors, this value predicts a fourth allotropic form of solid oxygen to be found with a transition temperature below 17°K.

The count of the rotational entropy of hydrogen is complicated by the presence of the symmetric and antisymmetric kinds in a one to three ratio. The question has been raised by Giauque[8] whether the entropy of mixing of these two kinds should not be included, especially as the

two forms do not intercombine spectroscopically. Rodebush[9] has answered that there really is only one hydrogen and that although the two forms do not intercombine in their spectral relations, they do so by collision when given a sufficient length of time to reach equilibrium. It is comforting to know that it really makes no difference in the final result which method of counting is used. The entropy of hydrogen at 25°C. comes out to be 34.0[10], whether we consider it two kinds and include the entropy of mixing or one substance which will reach equilibrium if given time enough. This, in fact, must be,[11] as can be seen from the following:

$$S_{rot} = R \ln \frac{4\pi^2 IkT}{h^2} (3 + 1) + \frac{E_{rot}}{T}$$

(one substance Gibson and Heitler count) or

$$\begin{aligned} S_{rot} &= S_{anti} + S_{sym} + S_{mixing} \\ &= \frac{3}{4} R \ln \frac{4\pi^2 IkT}{h^2} 3 + \frac{1}{4} R \ln \frac{4\pi^2 IkT}{h^2} - \frac{1}{4} R \ln \frac{1}{4} \\ &\qquad - \frac{3}{4} R \ln \frac{3}{4} + \frac{E_{rot}}{T} \\ &= R \ln \frac{4\pi^2 IkT}{h^2} 4 + \frac{R_{rot}}{T}. \end{aligned}$$

The entropy of hydrogen was also calculated by a summation process to check against possible inaccuracies introduced by the integration of the rotational sum. The results were identical.

The entropy of OH was next computed. As this molecule does not give rise to nuclear degeneracy the number of rotational terms is not halved as in the case of hydrogen and oxygen and the rotational entropy is expressed by the formula:

$$S_{rot} = R \ln 8\pi^2 IkT/h^2 + E_{rot}/T.$$

In addition to this rotational entropy comes entropy to account for the electronic states in the $^2P$ inverted ground term, which was incorrectly accounted for by Bonhoeffer and Reichardt. This should be as follows:

$$S_{elec} = R \ln (4 + 2e^{-h\Delta\nu/kT}) + \frac{E_{elec}}{T}.$$

The upper doublet term is not negligible in the case of the OH molecule, nor is it of full weight.

Table 1 gives the numerical data used to calculate the entropy formulas given on the following page.

TABLE 1

| | I | $\omega_0$ | $\Delta\nu$ |
|---|---|---|---|
| Hydrogen | $4.67 \times 10^{-41}$ g. cm.$^2$ | 4415.2 cm.$^{-1}$ | |
| Oxygen | $19.2 \times 10^{-40}$ | 1565.4 | |
| Hydroxyl | $1.43 \times 10^{-40}$ | 3570 | 137.9 cm.$^{-1}$ |

$$S_{O_2} = 13.70 + 11.52 \log T - 4.61 \log (1 - e^{-747.5/T}) + \frac{5}{2} R - 4.61 \log p_{atm} + \frac{E_{O_2}}{T}$$

$$S_{H_2} = -1.51 + 11.52 \log T - 4.61 \log (1 - e^{-6323/T}) + \frac{5}{2} R - 4.61 \log p_{atm} + \frac{E_{H_2}}{T}$$

$$S_{OH} = 5.77 + 11.52 \log T - 4.61 \log (1 - e^{-5112/T}) + 4.61 \log (4 + 2e^{-197.5/T}) + \frac{5}{2} R - 4.61 \log p_{atm} + \frac{E_{OH}}{T}.$$

From these values and the free energy formulas from Lewis and Randall,

$$\Delta F^\circ_{H_2O\ gas} = -57410 + 0.94\ T \ln T + 0.00165\ T^2 - 0.00000037\ T^3 + 3.92\ T$$
(Lewis and Randall, 485)

$$\Delta F^\circ_{H_2O_2\ gas} = -31200 + 5.5\ T \ln T - 0.00115\ T^2 - 9.3\ T$$
(Lewis and Randall, 496)

the equilibrium constants of the following reactions were calculated:

| | |
|---|---|
| $2OH = H_2 + O_2$ | (1) $K_1 = \dfrac{[H_2]\,[O_2]}{[OH]^2}$ |
| $2\,H_2O = 2H_2 + O_2 - 114$ k. cal. | (2) $K_{O_2} = \dfrac{[H_2]^2\,[O_2]}{[H_2O]^2}$ |
| $2\,H_2O = H_2 + 2OH$ | (3) $K_{OH} = \dfrac{[H_2][OH]^2}{[H_2O]^2}$ |
| $2\,OH = H_2O_2$ | (4) $K_4 = \dfrac{[H_2O_2]}{[OH]^2}$. |

The results are given in table 2, in which the subscripts $B$ denote that Bonhoeffer and Reichardt's values of the heat of dissociation of water were used and the subscripts $V$ denote that my value was used.

TABLE 2

| TEMPERATURE ABS. | LOG $K_{O_2}$ L AND R, p. 485 | LOG $K_{O_2}$ B AND R, p. 96 | LOG $K_{OH_B}$ | LOG $K_{OH}$ B AND R, p. 96 | LOG $K_{OH_V}$ | LOG $K_{1B}$ | LOG $K_{1V}$ | LOG $K_{tB}$ | LOG $K_{tV}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1000 | −19.8 | −20.1 | −21.8 | −21.1 | −15.5 | +1.95 | −4.35 | +2.74 | −3.55 |
| 1300 | −13.9 | −14.01 | −15.2 | −14.3 | −10.34 | +1.31 | −3.53 | +0.30 | −4.54 |
| 1500 | −11.2 | −11.42 | −12.24 | −11.4 | − 8.05 | +1.03 | −3.16 | −0.79 | −4.98 |
| 1705 | − 9.13 | − 9.28 | − 9.95 | − 9.0 | − 6.26 | +0.81 | −2.87 | −1.66 | −5.35 |
| 1900 | − 7.55 | − 7.6 interp. | − 8.21 | − 7.2 | − 4.90 | +0.65 | −2.66 | −2.29 | −5.60 |
| 2155 | − 5.94 | − 6.08 | − 6.42 | − 5.5 | − 3.50 | +0.48 | −2.43 | −2.99 | −5.91 |
| 2505 | − 4.27 | − 4.31 | − 4.59 | − 3.5 | − 2.08 | +0.32 | −2.19 | −3.67 | −6.18 |

$$2OH \longrightarrow H_2 + O_2 + 14{,}000 \text{ cal. } (B)$$
$$2OH \longrightarrow H_2 + O_2 - 15{,}000 \text{ cal. } (V)$$

[1] Villars, *J. Am. Chem. Soc.*, **51**, 2374–7 (1929).

[2] Dr. Langmuir has kindly pointed out that the knowledge of such equilibrium constants will be extremely useful in investigating the possibility of the direct formation of hydroxyl during the combustion of hydrogen and oxygen at high temperatures, an investigation which he is at present carrying on.

[3] *Z. physik. Chem.*, **139A**, 75–97 (1928).

[4] *Z. Physik*, **49**, 465.

[5] Cf. Rodebush's chapter XVII, p. 1202, in Taylor, *A Treatise on Physical Chemistry*, D. Van Nostrand, **1925.**

[6] Lewis and Gibson, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

[7] Mulliken, *Phys. Rev.*, **32**, 186.

[8] *J. Am. Chem. Soc.*, **50**, 3221.

[9] These PROCEEDINGS, **15**, 678–680 (1929).

[10] Rodebush, loc. cit., obtained this value and showed that the experimental method used to determine the entropy of hydrogen is theoretically unsound.

[11] Prof. Rodebush has shown independently that this relation must obtain.

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## *ON THE CRYSTAL STRUCTURE OF THE CHLORIDES OF CERTAIN BIVALENT ELEMENTS*

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Communicated August 6, 1929

In 1925 Bruni and Ferrari[1] reported that the lines on a powder photograph of the hexagonal crystal $MgCl_2$ could be accounted for on the basis of a rhombohedral (pseudocubic) unit of structure with $a = 5.08$ Å and $\alpha = 90^\circ$ containing 2 $MgCl_2$. Later they announced[2] that $ZnCl_2$, $CdCl_2$, and $MnCl_2$ have the same structure, with values of $\alpha$ a few degrees larger than $90^\circ$. Ferrari[3] then added $CoCl_2$ and $NiCl_2$ to the group; certain weak lines occurring on the powder photographs of these substances require the value of $a$ to be doubled, giving a rhombohedral unit with $\alpha = 90°$

and $a = 10.02$ Å and 10.00 Å, respectively, containing 16 $M^{++}Cl_2$. Goldschmidt[4] has also reported that unpublished powder photographic data obtained by Oftedal in his laboratory show that $RuCl_2$, $RhCl_2$, $PdCl_2$, $IrCl_2$, and $PtCl_2$ are to be assigned the same structure as $NiCl_2$.

None of these investigators succeeded in deducing the atomic arrangement in these crystals; the utilization of Bruni and Ferrari's data to this end is described in the following paragraphs.

Bruni and Ferrari published reproductions[2] of Laue photographs of $CdCl_2$, $MgCl_2$ and $MnCl_2$, taken in order to determine the axial ratios for these crystals. I have assigned indices to the spots appearing on the best of these photographs, that of $CdCl_2$, with the aid of a gnomonic projection made from a tracing. The forms producing these spots and values of $n\lambda$ calculated for a unit with $\alpha = 94°$ and $a = 10.2$ Å (an estimated value, about equal to that for $ZnCl_2$) are given in the first and second columns of table 1.

Only a few forms show $n\lambda$ values below 0.4 Å, indicating first-order reflections. It is, indeed, possible to account for the production of all of the spots on the photograph on the basis of a much smaller unit, a rhombohedron with $a = 6.35$ Å and $\alpha = 36° 40'$, containing $1MCl_2$. This unit has lattice points at the face-centered positions of the rhombohedron which is itself formed by the face-centered positions of the original pseudocubic unit. Inasmuch as values of $n\lambda$ calculated for this unit (fourth column of table 1) in no case fall below the short wave-length limit, the unit may be accepted as the true one.

The presence of a three-fold axis and three planes of symmetry in the Laue photograph taken with the incident beam normal to the basal plane requires that the crystal be isomorphous with one of the point-groups $C_{3v}$, $D_3$ and $D_{3d}$. The fundamental lattice has been found to be rhombohedral. The only ways of placing $1CdCl_2$ in the unit compatible with these restrictions are

I Cd at 000, 2 Cl at uuu, ūūū; $D_3^7$ and $D_{3d}^5$;
II Cd at $\frac{111}{222}$, 2 Cl at uuu, ūūū; $D_3^7$ and $D_{3d}^5$;
III Cd at uuu, $Cl_I$ at vvv, $Cl_{II}$ at www; $C_{3v}^5$.

In the absence of any evidence requiring it, the three-parameter structure III need not be considered.

Structures I and II are identical. The data are not sufficient for an accurate determination of the value of the chlorine parameter u. The fact that the powder photograph of $MgCl_2$ is nearly identical with that of LiCl indicates that the chlorine atoms are in nearly the same positions in the two crystals, namely, at the points of a face-centered cubic lattice. This corresponds to a value of u of $1/4$. Further evidence that the chloride

ions are in approximate cubic close-packing is provided by the consideration of interionic distances. With a crystal radius of 1.81 Å,[5] 32 chloride ions would occupy a cube 10.24 Å on an edge; this approximates closely the values reported for the various bivalent chlorides.

TABLE 1

DATA FROM BRUNI AND FERRARI'S LAUE PHOTOGRAPH OF CADMIUM CHLORIDE

| PSEUDOCUBIC UNIT $a = 10.2$ Å $\alpha = 94°$ | | TRUE UNIT $a = 6.36$ Å, $\alpha = 36°40'$ | | ESTIMATED INTENSITY* | STRUCTURE FACTOR |
|---|---|---|---|---|---|
| $\{hkl\}$ | $n\lambda$ | $\{hkl\}$ | $n\lambda$ | | |
| $33\bar{5}$ | 0.33 Å | $11\bar{1}$ | 0.33 Å | m. | $\overline{Cd} - 2\overline{Cl}$ |
| $3\bar{3}1$ | 0.68 | $21\bar{1}$ | 0.34 | w. | $\overline{Cd} - 2\overline{Cl}$ |
| $55\bar{7}$ | 0.40 | $22\bar{1}$ | 0.40 | m. | $\overline{Cd}$ |
| $12\bar{2}$ | 1.44 | $32\bar{1}$ | 0.36 | m.s. | $\overline{Cd} + 2\overline{Cl}$ |
| $77\bar{9}$ | 0.32 | $33\bar{1}$ | 0.32 | v.w. | $\overline{Cd}$ |
| $3\bar{2}0$ | 1.04 | 411 | 0.26 | v.w. | $\overline{Cd} - 2\overline{Cl}$ |
| $7\bar{3}1$ | 0.72 | 631 | 0.36 | v.w. | $\overline{Cd} - 2\overline{Cl}$ |
| $4\bar{1}\bar{1}$ | 1.52 | 611 | 0.38 | m. | $\overline{Cd} + 2\overline{Cl}$ |
| $4\bar{3}2$ | 1.40 | 750 | 0.35 | m.w. | $\overline{Cd} + 2\overline{Cl}$ |
| $6\bar{1}\bar{1}$ | 1.40 | 10.3.3 | 0.35 | v.v.w. | $\overline{Cd} + 2\overline{Cl}$ |
| $11\bar{1}$ | 4.44 | 110 | 2.22 | m. | |
| $3\bar{1}\bar{1}$ | 1.38 | 100 | 1.38 | s. | |
| $3\bar{1}0$ | 2.64 | 521 | 0.66 | m. | |
| $3\bar{2}1$ | 2.02 | 530 | 0.50 | m.w. | |
| $5\bar{1}\bar{1}$ | 1.52 | 411 | 0.76 | v.v.w. | |
| $5\bar{3}1$ | 1.20 | 210 | 1.20 | w. | |
| $7\bar{5}3$ | 0.80 | 320 | 0.80 | m.w. | |

* v.s. = very strong, m = medium, w = weak, etc.

Structure factors calculated for structure I with $u = 0.25$ are included in table 1 for forms giving first-order reflections. (These forms are arranged in order of decreasing interplanar distance.) These are in satisfactory agreement with intensities estimated from the reproduction of the photograph. Similar agreement is obtained with the powder photograph intensities for $MgCl_2$, $ZnCl_2$, $CoCl_2$ and $NiCl_2$ reported by Bruni and Ferrari.[6]

The structure found for this series of divalent chlorides is shown in the figure. It is a layer structure closely related to that of cadmium iodide. Each cation is surrounded by six chloride ions approximately at the corners of a regular octahedron, six edges of which are shared with other octahedra in such a way as to form a layer. In the cadmium iodide structure these layers are superimposed in such a way that each cation is directly above a cation in the layer below, whereas in the cadmium chloride structure each cation is directly above an anion in the layer below, and below an anion in the layer above. It is probable that the cadmium chloride structure is stable for substances $MX_2$ in which the cation $M$ has a coördination number 6 and the anion has an appreciable but not great polarizability.

I propose to carry on the experimental investigation of some of these crystals in order to obtain accurate values for the parameter. The discussion of interionic distances can be postponed until the results of this study are reported in the *Zeitschrift für Kristallographie*.

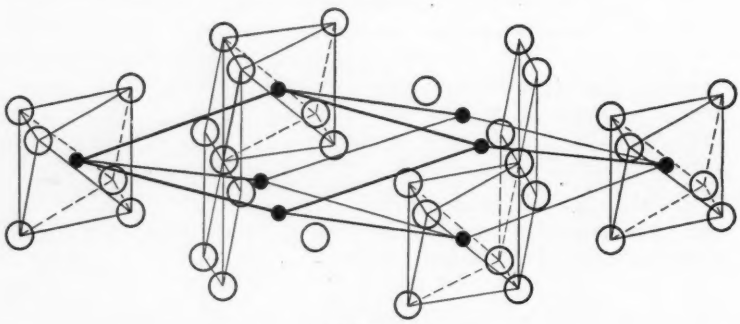

FIGURE I

The structure of cadmium chloride and other bivalent chlorides. Large open circles represent chloride ions, small closed circles cadmium ions. Heavy lines mark the rhombohedral unit of structure, and light lines the coördinated octahedron formed by six chloride ions about each cadmium ion.

*Summary.*—With the aid of data obtained from a reproduction of a Laue photograph published by Bruni and Ferrari, it is shown that the unit of structure of $CdCl_2$ is a rhombohedron with $\alpha = 36° 40'$ and $a = 6.35$ Å, about, containing $1CdCl_2$, Cd at 000, 2Cl at uuu, ūūū, with $u = 1/4$. The isomorphous crystals $MgCl_2$, $CoCl_2$, and $NiCl_2$ have $\alpha = 33° 36'$ and $a = 6.21$, 6.14 and 6.13 Å, respectively. Other representatives of the structure are $MnCl_2$, $ZnCl_2$, $RuCl_2$, $RhCl_2$, $PdCl_2$, $IrCl_2$ and $PtCl_2$.

[1] G. Bruni and A. Ferrari, *Rendiconti Acc. dei Lincei*, **2**, 457 (1925).

[2] G. Bruni and A. Ferrari, *Ibid.*, **4**, 10 (1926).

[3] A. Ferrari, *Ibid.*, **6**, 56 (1927).

[4] V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, VIII, p. 147.

[5] L. Pauling, *J. Am. Chem. Soc.*, **49**, 765 (1927).

[6] One line of small intensity, assigned indices {422} by Ferrari, is not compatible with the unit containing $1MCl_2$.

# THE ELASTIC PROPERTIES OF CERTAIN BASIC ROCKS AND OF THEIR CONSTITUENT MINERALS

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The rapid growth of the science of seismology, providing as it does more and more reliable data on the velocity of elastic waves at various depths within the Earth, calls for a closer study of the elastic constants of rocks and minerals because, given an accurate knowledge of the velocity of earthquake propagation at any depth and the elastic constants of all rocks under conditions prevailing at that depth, it is possible to speculate intelligently upon the nature of the rocks within the interior of the Earth.

Several years ago it was shown[1] that measurements of compressibility taken with the value of Poisson's ratio, which is approximately the same for all rocks, provided one of the best means of determining these elastic constants at high pressures. At that time the acidic rocks were investigated more thoroughly than the basic ones, and yielded more consistent results. The importance which is now being attached to the properties of basic rocks in inquiries concerning the nature of the deeper parts of the Earth's crust has made it seem advisable to carry out additional measurements of the compressibility of these rocks and certain of their constituent minerals.

In this work we have measured the compressibility of several diabases‡ with an improved apparatus, and where necessary redetermined the compressibility of the minerals in order to formulate more clearly the relation between the compressibility of the rocks and of their minerals. Furthermore, we have examined the compressibility of the garnets, grossularite and almandite, and of the pyroxene, jadeite, with a view to estimating the compressibility of eclogites, or rocks resembling basalt in gross composition but crystallized as high pressure minerals.

*Experimental Method.*—The apparatus, although entirely new, is very similar in construction to that already described in former publications[1] from this Laboratory. A leak-proof piston[2] is forced into a heavy-walled steel cylinder, which contains the specimen completely immersed in a suitable liquid (*n*-butyl ether). The hydrostatic pressure so generated is measured to 1 megabarye (about 1 atmosphere) by an electrical resistance gauge, and the corresponding decrease in volume is determined by measuring the travel of the piston with a dial-micrometer on which one division represents 0.01 mm. The apparatus is calibrated frequently by making a series of measurements on soft steel, the compressibility of which is accurately known.[3] The formula for calculating the decrease in volume for each pressure has been given fully in previous papers.[4]

*Materials.*—The sample of **Whin Sill diabase** was collected by Professor A. Holmes at Scordale Beck, near the Hilton lead mines, Westmorland, England. The rock is a fine-grained quartz-dolerite of density 2.937 at 31.4°. It has been described by Holmes and Harwood,[5] who give on page 512 of their paper a complete analysis. The calculated mode is approximately as follows: quartz, 7; plagioclase ($Ab_1An_1$), 47; augite, 19; hypersthene, 18; magnetite and ilmenite, 9.

TABLE 1

RESULTS FOR MINERALS

| PRESSURE (MEGABARYES) | ALMANDITE (243) $\phi 10^{4}a = -0.4$, $10^{4}b = 0.576$ | | | ALMANDITE (241) $10^{4}a = 0.4$, $10^{4}b = 0.557$ | | | GROSSULARITE (239) $10^{4}a = 1.2$, $10^{4}b = 0.600$ | | | GROSSULARITE (245) $10^{4}a = 2.1$, $10^{4}b = 0.595$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ |
| 12000 | 0.565 | 0.572 | −0.7 | 0.550 | 0.561 | −1.1 | 0.601 | 0.613 | −1.2 | 0.606 | 0.616 | −1.0 |
| 11000 | 0.517 | 0.515 | 0.2 | 0.506 | 0.505 | 0.1 | 0.550 | 0.553 | −0.3 | 0.556 | 0.556 | 0.0 |
| 10000 | 0.455 | 0.457 | −0.2 | 0.456 | 0.450 | 0.6 | 0.489 | 0.493 | −0.4 | 0.494 | 0.497 | −0.3 |
| 9000 | 0.404 | 0.399 | 0.5 | 0.397 | 0.394 | 0.3 | 0.435 | 0.433 | 0.2 | 0.437 | 0.437 | 0.0 |
| 8000 | 0.347 | 0.342 | 0.5 | 0.349 | 0.338 | 1.1 | 0.382 | 0.373 | 0.9 | 0.372 | 0.378 | −0.6 |
| 7000 | 0.287 | 0.284 | 0.3 | 0.288 | 0.283 | 0.5 | 0.315 | 0.313 | 0.2 | 0.332 | 0.318 | 1.4 |
| 6000 | 0.231 | 0.227 | 0.4 | 0.228 | 0.227 | 0.1 | 0.263 | 0.253 | 1.0 | 0.263 | 0.259 | 0.4 |
| 5000 | 0.166 | 0.169 | −0.3 | 0.165 | 0.171 | −0.6 | 0.207 | 0.193 | 1.4 | 0.208 | 0.199 | 0.9 |
| 4000 | 0.098 | 0.111 | −1.3 | 0.117 | 0.116 | 0.1 | 0.141 | 0.132 | 0.9 | 0.161 | 0.140 | 2.1 |
| 3000 | 0.055 | 0.054 | 0.1 | 0.054 | 0.060 | −0.6 | 0.055 | 0.072 | −1.7 | (0.109)* | (0.080)* | ... |
| 2000 | 0.000 | −0.004 | 0.4 | 0.000 | 0.004 | −0.4 | 0.000 | 0.012 | −1.2 | 0.000 | 0.021 | −2.1 |

| PRESSURE (MEGABARYES) | GROSSULARITE (261)+ $10^{4}a = 3.8$, $10^{4}b = 0.611$ | | | JADEITE (251) $10^{4}a = 1.6$, $10^{4}b = 0.735$ | | | JADEITE (249) $10^{4}a = 3.1$, $10^{4}b = 0.775$ | | | LABRADORITE (235) $10^{4}a = 0.2$, $10^{4}b = 1.457$, $10^{10}c = -0.115$ | | | LABRADORITE (237) $10^{4}a = 0.1$, $10^{4}b = 1.417$, $10^{10}c = -0.086$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ | $-\frac{\Delta V}{V_o} \times 10^{2}$ (OBS.) | $-\frac{\Delta V}{V_o} \times 10^{2}$ (CALC.) | DIFF. $\times 10^{4}$ |
| 12000 | 0.642 | 0.649 | −0.7 | 0.748 | 0.751 | −0.3 | 0.784 | 0.806 | −2.2 | 1.342 | 1.344 | −0.2 | 1.328 | 1.333 | −0.5 |
| 11000 | 0.591 | 0.588 | 0.3 | 0.669 | 0.678 | −0.9 | 0.715 | 0.729 | −1.4 | 1.225 | 1.220 | 0.5 | 1.211 | 1.208 | 0.3 |
| 10000 | 0.524 | 0.527 | −0.3 | 0.603 | 0.604 | −0.1 | 0.659 | 0.651 | 0.8 | 1.101 | 1.094 | 0.7 | 1.092 | 1.081 | 1.1 |
| 9000 | 0.470 | 0.466 | 0.4 | 0.531 | 0.531 | 0.0 | 0.579 | 0.574 | 0.5 | 0.959 | 0.966 | −0.7 | 0.946 | 0.952 | −0.6 |
| 8000 | 0.409 | 0.405 | 0.4 | 0.460 | 0.457 | 0.3 | 0.508 | 0.496 | 1.2 | 0.830 | 0.835 | −0.5 | 0.818 | 0.821 | −0.3 |
| 7000 | 0.351 | 0.344 | 0.7 | 0.391 | 0.384 | 0.7 | 0.439 | 0.419 | 2.0 | 0.693 | 0.702 | −0.9 | 0.683 | 0.689 | −0.6 |
| 6000 | 0.276 | 0.282 | −0.6 | 0.312 | 0.310 | 0.2 | 0.352 | 0.341 | 1.1 | 0.569 | 0.566 | 0.3 | 0.556 | 0.555 | 0.1 |
| 5000 | 0.217 | 0.221 | −0.4 | 0.243 | 0.237 | 0.6 | 0.276 | 0.264 | 1.2 | 0.444 | 0.429 | 1.5 | 0.426 | 0.419 | 0.7 |
| 4000 | ... | ... | ... | 0.178 | 0.163 | 1.5 | 0.192 | 0.186 | 0.6 | 0.286 | 0.289 | −0.3 | 0.278 | 0.282 | −0.4 |
| 3000 | ... | ... | ... | 0.083 | 0.090 | −0.7 | 0.104 | 0.109 | −0.5 | 0.144 | 0.146 | −0.2 | 0.146 | 0.143 | 0.3 |
| 2000 | ... | ... | ... | 0.000 | 0.016 | −1.6 | 0.000 | 0.031 | −3.1 | 0.000 | 0.002 | −0.2 | 0.000 | 0.001 | −0.1 |

* Omitted from the least square calculation.

The **Maryland diabase** was collected by Dr. E. S. Shepherd on the Baltimore Pike near Frederick, Md. It is a fine-grained diabase, density 3.033 at 31.0°. An unpublished analysis, by E. S. Shepherd, of the specimen used in this work is as follows: $SiO_2$, 51.28; $Al_2O_3$, 15.07; $Fe_2O_3$, 1.12; FeO, 9.31; MgO, 7.97; CaO, 11.42; $Na_2O$, 2.03; $K_2O$, 0.27; $H_2O$ +, 0.39; $H_2O$−, 0.09; $TiO_2$, 0.78; $P_2O_5$, 0.13; Cl, 0.00; S, 0.06; $Cr_2O_3$, 0.05; MnO, 0.16. Calculated mode; plagioclase ($Ab_1An_2$), 48; augite, 24; hypersthene, 25; magnetite and ilmenite, 3.

The specimen of **Sudbury diabase** is the same as that used by Adams and Williamson.[6] Density 3.002 at 31.1°. It is a moderately coarse-

grained olivine diabase. Calculated mode: plagioclase ($Ab_3An_2$), 60; augite, 15; olivine, 17; magnetite and ilmenite, 8.

The **jadeite** was from a large piece of massive material from Burma and was kindly furnished by Dr. W. F. Foshag of the U. S. National Museum. Density 3.328 at 30.9°. Microscopic analysis showed it to be practically pure jadeite.

The fine specimen of translucent massive **grossularite** was also furnished by Dr. Foshag. Density 3.544 at 30.9°. An analysis of material from the locality has been made by Clarke and Steiger.[7]

TABLE 2

RESULTS FOR DIBASE ROCKS

| PRESSURE (MEGABARYES) | MARYLAND DIABASE (227) $10^4a = -0.23$, $10^4b = 1.280$, $10^{10}c = -0.115$ | | | MARYLAND DIABASE (229) $10^4a = 0.35$, $10^4b = 1.239$, $10^{10}c = -0.135$ | | | MARYLAND DIABASE (233) $10^4a = 0.21$, $10^4b = 1.228$, $10^{10}c = -0.130$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ |
| 12000 | 1.164 | 1.162 | 0.2 | 1.111 | 1.107 | 0.4 | 1.103 | 1.100 | 0.3 |
| 11000 | 1.048 | 1.056 | −0.8 | 1.007 | 1.009 | −0.2 | 1.005 | 1.002 | 0.3 |
| 10000 | 0.958 | 0.948 | 1.0 | 0.911 | 0.908 | 0.3 | 0.903 | 0.901 | 0.2 |
| 9000 | 0.835 | 0.837 | −0.2 | 0.797 | 0.804 | −0.7 | 0.787 | 0.798 | −1.1 |
| 8000 | 0.722 | 0.724 | −0.2 | 0.694 | 0.698 | −0.4 | 0.683 | 0.692 | −0.9 |
| 7000 | 0.604 | 0.609 | −0.5 | 0.582 | 0.589 | −0.7 | 0.585 | 0.584 | 0.1 |
| 6000 | 0.493 | 0.491 | 0.2 | 0.483 | 0.477 | 0.6 | 0.477 | 0.473 | 0.4 |
| 5000 | 0.374 | 0.371 | 0.3 | 0.371 | 0.363 | 0.8 | 0.375 | 0.359 | 1.4 |
| 4000 | 0.252 | 0.249 | 0.3 | 0.254 | 0.246 | 0.8 | 0.240 | 0.243 | −0.3 |
| 3000 | 0.118 | 0.125 | −0.7 | 0.120 | 0.126 | −0.6 | 0.119 | 0.124 | −0.5 |
| 2000 | 0.000 | −0.002 | 0.2 | 0.000 | 0.004 | −0.4 | 0.000 | 0.002 | −0.2 |

| PRESSURE (MEGABARYES) | SUDBURY DIABASE (217) $10^4a = 0.13$, $10^4b = 1.440$, $10^{10}c = -0.130$ | | | SUDBURY DIABASE (219) $10^4a = 0.05$, $10^4b = 1.351$, $10^{10}c = -0.061$ | | | WHIN SILL DIABASE (221) $10^4a = 0.15$, $10^4b = 1.712$, $10^{10}c = -0.284$ | | | WHIN SILL DIABASE (223). $10^4a = 0.58$, $10^4b = 1.688$, $10^{10}c = -0.280$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ | $-\frac{\Delta V}{V_o} \times 10$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ | $-\frac{\Delta V}{V_o} \times 10^3$ (OBS.) | (CALC.) | DIFF. $\times 10^4$ |
| 12000 | 1.317 | 1.312 | 0.5 | 1.295 | 1.291 | 0.4 | 1.434 | 1.430 | 0.4 | 1.418 | 1.414 | 0.4 |
| 11000 | 1.182 | 1.192 | −1.0 | 1.163 | 1.168 | −0.5 | 1.309 | 1.312 | −0.3 | 1.299 | 1.298 | 0.1 |
| 10000 | 1.080 | 1.070 | 1.0 | 1.048 | 1.043 | 0.5 | 1.192 | 1.189 | 0.3 | 1.181 | 1.177 | 0.4 |
| 9000 | 0.941 | 0.946 | −0.5 | 0.911 | 0.917 | −0.6 | 1.054 | 1.061 | −0.7 | 1.040 | 1.050 | −1.0 |
| 8000 | 0.816 | 0.819 | −0.3 | 0.784 | 0.790 | −0.6 | 0.929 | 0.927 | 0.2 | 0.906 | 0.918 | −1.2 |
| 7000 | 0.683 | 0.689 | −0.6 | 0.659 | 0.661 | −0.2 | 0.773 | 0.787 | −1.4 | 0.774 | 0.780 | −0.6 |
| 6000 | 0.563 | 0.557 | 0.6 | 0.537 | 0.531 | 0.6 | 0.648 | 0.638 | 1.0 | 0.644 | 0.636 | 0.8 |
| 5000 | 0.428 | 0.422 | 0.6 | 0.407 | 0.400 | 0.7 | 0.498 | 0.490 | 0.8 | 0.502 | 0.487 | 1.5 |
| 4000 | 0.282 | 0.284 | −0.2 | 0.270 | 0.268 | 0.2 | 0.341 | 0.333 | 0.8 | 0.339 | 0.332 | 0.7 |
| 3000 | 0.143 | 0.144 | −0.1 | 0.130 | 0.135 | −0.5 | 0.161 | 0.170 | −0.9 | 0.166 | 0.172 | −0.6 |
| 2000 | 0.000 | 0.001 | −0.1 | 0.000 | 0.001 | −0.1 | 0.000 | 0.001 | −0.1 | 0.000 | 0.006 | −0.6 |

The **almandite,** from Salida, Col., was also furnished by Dr. Foshag. Density 4.160 at 30.9°. An analysis of almandite from the same locality has been made by Penfield and Sperry.[8]

The specimen of **labradorite,** from Nain, Labrador, is the same as that described in a previous paper.[6] The density is 2.696 at 29.5°, and the composition is approximately $Ab_{48}An_{52}$.

*Experimental Results.*—The results for the three rocks and for the four minerals are shown in tables 1 and 2, which give the fractional decrease

in volume, $-\Delta V/V_o$, caused by an increase of pressure from 2000 megabaryes to the pressure indicated. Within the experimental error, the observations for jadeite and for the two garnets, fall on a straight line, when $\Delta V/V_o$ is plotted against the pressure, $P$. Accordingly, they have been represented by the equation:

$$-\Delta V/V_o = a + b\,(P - 2000) \qquad (1)$$

where $a$ and $b$ are constants. These constants were calculated from the data by the method of least squares, and are shown in table 1 at the head of each series of results. The agreement between the observed values of $\Delta V/V_o$ and those calculated by equation (1) is quite satisfactory and indicates that the readings of the dial-micrometer were consistent to better than 0.01 mm.

For labradorite the graph of $\Delta V/V_o$ against $P$ is distinctly curved; the results, therefore, are represented by a quadratic equation:

$$-\Delta V/V_o = a + b\,(P - 2000) + c\,(P - 2000)^2 \qquad (2)$$

the constants, $a$, $b$, and $c$ being obtained from a least-square solution.

The compressibility, $\beta$(equal to $-\mathrm{d}V/V_o\ \mathrm{d}P$) may be obtained by differentiating equation (1) or (2). The compressibility of **labradorite** varies considerably with pressure, and is found to be $\mathbf{1.48 \times 10^{-6}}$ at $P = 0$, and $\mathbf{1.28 \times 10^{-6}}$ at $P = 10{,}000$ megabaryes. These values are somewhat lower than those previously obtained (1.55 and 1.34, respectively), but the difference is partly accounted for by the lower value now taken for the compressibility of the reference substance, soft steel.

The compressibilities of the minerals are summarized in table 3, in which have also been inserted the results previously obtained for other minerals commonly found in basic rocks and the observations on magnetite and ilmenite made by Madelung and Fuchs.[9] For those substances, whose change of compressibility has not been measured, the compressibilities at the various pressures have been determined by the empirical method already described.[10] This method takes advantage of the fact that, approximately, the change of compressibility with pressure is a function of the compressibility alone. If the compressibility at only one pressure, or the mean compressibility over a certain range of pressure, is known, the compressibility at various pressures can be estimated, probably with considerable accuracy, and certainly with less error than if no allowance were made for the change of compressibility.

In the plagioclase series only two members have been investigated, but on the assumption that the compressibility bears a linear relation to the volume-percentage of albite or anorthite the compressibilities of two other members of the series, $Ab_{60}An_{40}$ and $Ab_{33}An_{67}$, have been calculated. In table 3 those values which have been obtained by interpolation,

extrapolation, or correction for the "statistical" change of compressibility are enclosed in parentheses. For pressures from 0 to 15,000 megabaryes, this table gives a comprehensive view of the compressibilities of the more important minerals found in basic rocks.

TABLE 3

COMPRESSIBILITIES OF THE IMPORTANT MINERALS IN BASIC ROCKS

| MINERAL | COEFFS. OF EQUATIONS (1) AND (2) $10^6 b$ | $-10^{10} c$ | COMPRESSIBILITY, $10^6\beta$, AT THE FOLLOWING PRESSURES (MEGABARYES) 0 | 2000 | 7000 | 10,000 | 15,000 |
|---|---|---|---|---|---|---|---|
| Quartz | 2.61 | 0.216 | 2.70 | 2.61 | 2.40 | 2.27 | .. |
| Oligoclase $Ab_{78}An_{22}$ | 1.70 | 0.105 | 1.74 | 1.70 | 1.60 | 1.54 | (1.44) |
| Andesine $Ab_{60}An_{40}$ | .. | ... | (1.59) | (1.55) | (1.45) | (1.39) | (1.29) |
| Labradorite $Ab_{48}An_{52}$* | 1.44 | 0.100 | 1.48 | 1.44 | 1.34 | 1.28 | (1.18) |
| Labradorite $Ab_{33}An_{67}$ | .. | ... | (1.32) | (1.30) | (1.24) | (1.20) | (1.14) |
| Actinolite | 1.29 | ... | (1.37) | (1.35) | 1.29 | (1.25) | (1.19) |
| Diopside | 1.06 | ... | (1.13) | (1.11) | 1.06 | (1.03) | (0.98) |
| Augite | 1.01 | ... | (1.07) | (1.05) | 1.01 | (0.98) | (0.94) |
| Enstatite | 1.00 | ... | (1.06) | (1.04) | 1.00 | (0.97) | (0.93) |
| Hypersthene | 0.98 | ... | (1.04) | (1.02) | 0.98 | (0.95) | (0.91) |
| Olivine | 0.81 | ... | (0.85) | (0.84) | 0.81 | (0.79) | (0.76) |
| Jadeite* | 0.75 | ... | (0.78) | (0.77) | 0.75 | (0.73) | (0.71) |
| Garnet (Grossularite)* | 0.60 | ... | (0.63) | (0.62) | 0.60 | (0.59) | (0.57) |
| Garnet (Almandite)* | 0.57 | ... | (0.60) | (0.59) | 0.57 | (0.56) | (0.54) |
| Ilmenite | .. | ... | 0.56 | (0.55) | (0.53) | (0.52) | (0.50) |
| Magnetite | .. | ... | 0.55 | (0.54) | (0.52) | (0.51) | (0.49) |

* New determinations described in this paper.

With each of the three rocks investigated the volume-decrease was not a linear function of the pressure, a fact which was at once evident from the graphs. Two series of measurements were made with the Whin Sill diabase, two with the Sudbury, and three with the Maryland. There seemed to be a tendency for the second or third series with a given specimen to yield a somewhat lower compressibility than the first series. This was probably due to the liquid more completely filling the fine pores of the rock by the continued application of pressure. In figure 1 is shown graphically the volume-change under pressure for the Whin Sill and for the Maryland diabase (two series for each).

*Discussion.*—In a previous investigation[6] the compressibility of rocks was measured under two different conditions, (1) the rock was placed directly in contact with the pressure-transmitting liquid, and (2) the rock was completely enclosed in a thin jacket of tin. The first method, leading to the "inner" compressibility, gave the volume changes due to the compression of the actual material particles of the rock because the pressure liquid had ample opportunity to fill up the interstices; but in the second method, from which the "outer" compressibility was calculated, the observed volume change included both the change due to the compression of the particles and that due to the closing of the pores.

If we are interested in the propagation of elastic waves through a rock of a certain composition and structure on the surface of the Earth the "outer" compressibility is the modulus which is of most importance to us, but in this paper we are more concerned with rocks formed under pressures at which a very compact structure would be most probable. For this reason and also on account of the greater ease of experimentation we have made all our measurements on unenclosed specimens. At lower pressures the differences between these two types of compressibility are

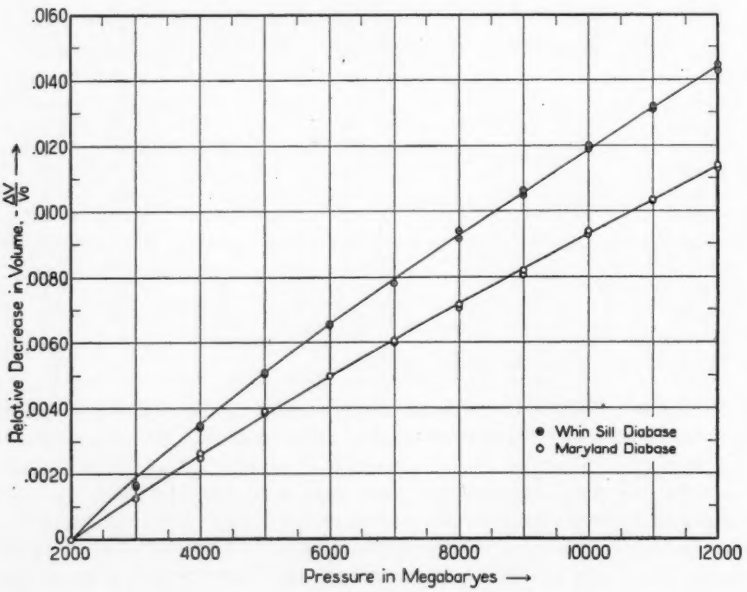


FIGURE 1

Final results for the volume change under pressure of Whin Sill and Maryland diabases.

considerable for many, especially the more porous rocks, but beyond 10,000 megabaryes the differences approach zero asymptotically and so our problem is simplified.

In the paper by Adams and Williamson[6] it is shown that at high pressures the compressibility of rocks tends toward the value obtained by averaging (according to volume-percentage) the compressibilities of the minerals present in the rock. At lower pressures, however, compressibility of the rock may be much greater than that calculated from the minerals and depends as much on the physical condition of the particular rock as on its mineral composition. Figure 2, which is taken (with minor changes) from

the earlier paper, illustrates the way in which the compressibilities of granitic and gabbroic rocks vary with pressure or depth. The large variation at low pressures depends on the more or less accidental structure of the rock, while at high pressures the variation is mainly that due to differences in mineral content of the rock of the type in question.

In table 4 are summarized, first the compositions of the various rocks in terms of the minerals present, and second the measured and calculated compressibilities at certain pressures. The results for the previously investigated Palisade diabase, recalculated to show the change of com-

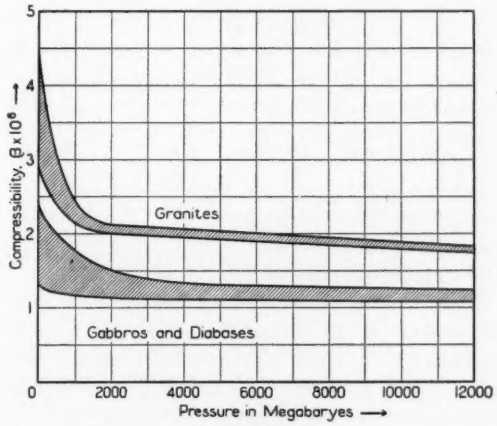


FIGURE 2

The compressibility of granites and diabases as a function of pressure. The width of the shaded areas indicates the variation which may be expected for ordinary rocks within a given class. At high pressures the variation is governed by the mineral composition of the rock, at low pressures the variation in compactness is the dominating factor.

pressibility with pressure, have been included in the table. There is also included the presumable mineral content and the calculated compressibility of the average plateau basalt as computed by R. A. Daly[11] from 50 analyses of Deccan, Oregonian and Thulean flows.

The measured compressibility, which at 2000 mb. exhibits a considerable variation from one rock to another, shows much less variation at 10,000 mb. Moreover, at 10,000 mb. the compressibilities have approached fairly closely to those calculated from the minerals, being on the average only $0.10 \times 10^{-6}$ higher. In one case—the Maryland diabase—the figures are the same for the measured and calculated compressibilities. The

greatest divergence is found for the Palisade diabase, the measured and calculated values being $1.30 \times 10^{-6}$ and $1.16 \times 10^{-6}$, respectively. It is significant in this connection that by one criterion of the degree of weathering the Maryland diabase is a much fresher rock than the Palisade diabase. According to unpublished measurements by E. S. Shepherd the latter yields 90 cm.$^3$ of gas (mostly water vapor) per gram when heated to a high temperature in a vacuum, while the former evolves only 30 cm.$^3$ per gram, which is close to the minimum observed for ordinary rocks. Only lavas from recent flows show less. In the former paper the presence of saussuritized feldspar in the Palisade diabase was noted as an indication

TABLE 4

COMPRESSIBILITY AND MINERAL COMPOSITION OF VARIOUS DIABASE ROCKS

| | WHIN SILL | SUDBURY | PALISADE | MARYLAND | AVERAGE PLATEAU BASALT (DALY) |
|---|---|---|---|---|---|
| MINERAL COMPOSITION | | | | | |
| Quartz | 7 | .... | .... | .... | .... |
| Plagioclase | 47 (1,1) | 60 (3,2) | 54 (3,2) | 48 (1,2) | 50 (3,2) |
| Augite | 19 | 15 | 20 | 24 | 37 |
| Hypersthene | 18 | .... | 14 | 25 | |
| Olivine | .... | 17 | 5 | .... | 4 |
| Magnetite and Ilmenite | 9 | 8 | 7 | 3 | 9 |
| COMPRESSIBILITY, $\beta \times 10^6$ | | | | | |
| Measured $P$ = 2000 mb. | 1.70 | 1.37 | 1.54 | 1.23 | .... |
| Measured $P$ = 10,000 mb. | 1.26* | 1.25* | 1.30* | 1.07* | .... |
| Calcd. from minerals $P$ = 10,000 mb. | 1.17 | 1.16 | 1.16 | 1.07 | 1.13 |
| Calcd. from minerals $P$ = 15,000 mb. | 1.09 | 1.08 | 1.09 | 1.02 | 1.06 |

* These figures were calculated by passing a least-square straight line through the points from 8000 to 12,000 megabaryes. It is noteworthy that the same result was obtained from the slope of the quadratic equation at 10,000 megabaryes.

that the rock was not perfectly fresh. The Maryland rock, on the other hand, is probably a very perfect specimen of a sound and fresh diabase. Even at 2000 megabaryes the measured compressibility is nearly as low as that calculated from the minerals (1.23 against 1.16). We may conclude from the table that at high pressures the compressibilities of the various rocks approach and finally become equal to those calculated from the mineral content. Indeed, it appears that for any rock a *minimum* value of its compressibility at any pressure may be obtained by averaging the compressibilities of its constituent minerals. The actual compressibility may be considerably higher, especially at low pressures. It is interesting that granites lose their abnormality almost entirely at 2000 mb. or less, but that the basic rocks in most instances still retain some of their abnormality even at 10,000 mb.

In a former paper a slightly higher value was assigned to the compressibility of diabase than will be found here. This is due to two factors: (1) better values now available for the compressibility of the standard of reference, steel, which are lower than those used in the previous work, and which exhibit an appreciable decrease with increasing pressure; and (2) the difference between the old and the new values for the compressibility of labradorite.

From figure 2 it may be seen that the characteristic course of the compressibility of rocks as the pressure is increased is first a rapid and then a much slower decrease of the compressibility. This course should properly be represented by an equation with an exponential term. Even though the volume change of a rock in the pressure-range from 2000 to 12,000 megabaryes may, within the error of experiment, follow a parabolic equation such as eqn. (2), it is very evident that an extrapolation by such an equation to either higher or lower pressures would be very unsafe. Indeed, an extrapolation in either direction would yield compressibilities lower than the true ones. At very low pressures the compressibility of a given sample of rock can be determined only by direct measurement on the particular sample, and at pressures above the experimental range a calculation based on the extrapolated compressibilities of the constituent minerals will give the most satisfactory value, although it is to be remembered that the value so obtained is merely the *minimum* compressibility. The bottom line of table 4 shows the calculated compressibilities at 15,000 megabaryes of the four diabases and also of Daly's average basalt (if crystalline). It does not seem possible that the compressibilities at the pressure stated can be significantly lower than the values given, and it does not seem probable that they can be very much higher.

In a recent paper on "The Outer Shells of the Earth," R. A. Daly[11] has made a painstaking criticism of all previous determinations of the compressibility of rocks, and has concluded that the values which have been given for the compressibilities are too high, mainly because of two factors: first, the change of compressibility with pressure; and second, the tendency of elastic hysteresis to increase the effective elastic moduli of rocks. The first effect has already been discussed in a paper by the authors, and as for the second, we have not been able to observe any hysteresis in the volume change of igneous rocks when subjected to *hydrostatic* pressure.

From the compressibilities given in table 4 the velocity of longitudinal waves through the various diabase rocks has been calculated by the equation:[6]

$$U_p = 13.13/\sqrt{10^6 \beta \rho}, \qquad (3)$$

where $U_p$ is the velocity in kilometers per second and $\rho$ is the density. The results are shown in the following table.

TABLE 5

VELOCITY OF LONGITUDINAL WAVES IN VARIOUS DIABASE ROCKS

| ROCK | VELOCITY IN KM./SEC. AT VARIOUS PRESSURES | | | |
|---|---|---|---|---|
| | 2000 $\beta$ MEASURED | 10,000 $\beta$ MEASURED | 10,000 $\beta$ CALC. | 15,000 $\beta$ CALC. |
| Whin Sill diabase | 5.9 | 6.8 | 7.0 | 7.3 |
| Sudbury diabase | 6.5 | 6.7 | 7.0 | 7.2 |
| Palisade diabase | 6.1 | 6.6 | 7.0 | 7.2 |
| Maryland diabase | 6.8 | 7.2 | 7.2 | 7.4 |
| Av. plateau basalt | ... | ... | 7.1 | 7.3 |

The velocities at 15,000 megabaryes equivalent to a depth of slightly more than 50 kilometers are appreciably less than 7.9 km. per sec., which is the velocity of longitudinal waves at this depth as deduced from seismologic data. It should be noted that the velocities given in table 5 apply only if the rock is crystalline. The compressibilities of glass and glassy rocks[4] will be discussed in a subsequent paper.

For plateau basalt the velocity at 15,000 megabaryes is 7.3 km./sec. Although the gap between 7.3 and 7.9 is not large, it seems difficult to close it and thus to allow crystalline basalt—with glassy basalt the gap is wider—at depths below the 50–60 km. discontinuity. We believe that the compressibility of diabase as here given cannot be in error by as much as 4 per cent, which would correspond to 2 per cent for the wave velocity. In order to have material of the composition of diabase below the 50–60 km. discontinuity it seems necessary to assume: (1) that that material is crystalline; (2) that the effect of temperature is negligible; and (3) that the seismologic value for the velocity at this depth is in error by at least 0.6 km./sec.

*The Compressibility of Eclogites.*—The compressibilities of grossularite and almandite, the only two garnets we could obtain as large cylinders, are given in table 1, and may be summarized by the statement that the average compressibility between 2000 and 12,000 megabaryes is $\mathbf{0.60 \times 10^{-6}}$ for **grossularite** and $\mathbf{0.57 \times 10^{-6}}$ for **almandite.** Although the compositions of these two garnets differ widely, their compressibilities are nearly the same and we are emboldened to place the average compressibility of pyrope between that of grossularite and almandite.

We also determined the compressibility of **jadeite.** The results are in table 1 and indicate that the average compressibility of this mineral is $\mathbf{0.75 \times 10^{-6}}$ reciprocal megabaryes.

With the help of these results it is possible to calculate the approximate compressibility of an eclogite. In table 6 we have taken hypothetical eclogites whose mineral compositions are based on three of the Norwegian eclogites so carefully studied by Eskola.[12] The compressibility of each has been calculated at 7000 megabaryes from our data and thence the earthquake wave velocity through such rocks has been obtained in the usual way. It must be emphasized that although we have tried to keep

the compositions of the hypothetical rocks within the bounds of plausibility these calculations must be regarded as approximate and are intended merely to assign probable elastic constants to rocks composed of high-pressure minerals. The wave velocities in these eclogite rocks even at 7000 megabaryes are about the same as those given below the 50–60 km. discontinuity by the seismic data, and hence our results do not conflict with the hypothesis[13] of an eclogite shell at that depth. Further discussion of this is postponed to some future occasion.

TABLE 6

CALCULATED COMPRESSIBILITIES AT 7000 MEGABARYES OF CERTAIN ECLOGITES AND THE VELOCITIES OF LONGITUDINAL WAVES THROUGH THEM

| PERCENTAGE BY VOLUME | | | AVERAGE | AVERAGE | AVERAGE | REFERENCE |
|---|---|---|---|---|---|---|
| GARNET | JADEITE | DIOPSIDE | $\rho$ | $\beta$ | $U_p$ | |
| 50 | 30 | 20 | 3.7 | 0.73 | 8.0 | 1 |
| 42 | 6 | 52 | 3.5 | 0.84 | 7.7 | 2 |
| 32 | 24 | 44 | 3.5 | 0.83 | 7.7 | 3 |

1 Analogous to chloromelanite eclogite from Vanelvsdalen, Søndmøre, cf. *Eskola*, p. 31.

2 Analogous to eclogite from Rødhaugen, Almklovdalen, Søndmøre, cf. *Eskola*, p. 27.

3 Analogous to eclogite from Silden, Nordfjord, cf. *Eskola*, p. 37.

*Summary and Conclusions.*—We have measured directly, at pressures between 2000 and 12,000 megabaryes, the cubic compressibility of the minerals, labradorite, jadeite, grossularite and almandite, and of diabase rocks from Sudbury, Canada; Frederick, Maryland; and the Whin Sill in the North of England. By combining these mineral results with those already known, we are able to give a table of the compressibilities, at various pressures, of all the important constituents of basic rocks, to compare the compressibilities of the rocks with those of their constituent minerals, and to conclude that the compressibility calculated from the mineral content gives a limit to which that of the rocks approaches at high pressure. Our results demonstrate, furthermore, that at 15,000 megabaryes and 30°C. the *maximum* velocity of longitudinal elastic waves through rocks of basaltic composition and mode is 7.4 km. per sec. On the other hand, the compressibilities of garnet and jadeite, being found to be surprisingly low, lead to the conclusion that magmas of this composition, crystallized primarily as, or subsequently metamorphosed to eclogites, may transmit longitudinal waves with velocities exceeding 8 km. per sec. Bearing in mind that the pressures existing at 20, 40 and 60 km. below the surface of the earth are somewhat greater than 5, 10 and 15 thousand megabaryes, respectively, we may readily see the connection between these observations and deductions concerning the composition of the interior of the earth. Indeed, the existing data, in our opinion, place the possible components of the earth, below 60 km. and above the core,

in the following ascending order of probability: holocrystalline basalt, eclogite, peridotite.

The authors are indebted to their colleagues, Drs. H. S. Washington, N. L. Bowen, J. W. Greig and E. S. Shepherd for many helpful suggestions, to Dr. W. F. Foshag for his aid in obtaining certain mineral specimens for this investigation, and to Professor A. Holmes for his kindness in collecting from the desired locality a sample of the Whin Sill diabase.

* Papers from the Geophysical Laboratory, Carnegie Institution of Washington, No. 690.

‡ Throughout this paper the word *diabase* is used in the American sense to indicate a holocrystalline basalt. It should be understood by British readers to mean *dolerite*.

[1] Adams, Williamson and Johnston, *J. Am. Chem. Soc.*, **41**, 1919 (12). Adams and Williamson, *J. Franklin Inst.*, **195**, 1923 (475).

[2] P. W. Bridgman, *Proc. Am. Acad. Arts & Sci.*, **49**, 1914 (634).

[3] P. W. Bridgman, *Proc. Am. Acad. Arts & Sci.*, **58**, 1923 (166); see also Adams and Gibson, These PROCEEDINGS, **12**, 1926 (275); *Gerlands Beitr. z. Geophys.*, **15**, 1926 (17).

[4] Adams and Gibson, *Op. cit.*; Adams and Williamson, *Op. cit.*

[5] Holmes and Harwood, *Min. Mag.*, **21**, 1928 (493).

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[7] Clarke and Steiger, *U. S. Geol. Surv., Bull.* No. **262**, 1905 (72).

[8] Penfield and Sperry, *Am. J. Sci.*, **32**, 1886 (311).

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[10] L. H. Adams, *J. Wash. Acad. Sci.*, **17**, 1927, 529.

[11] R. A. Daly, *Am. J. Sci.*, **15**, 1928 (108).

[12] Pentti Eskola. *Vidensk. Skrifter I. Mat. Nature.* Klasse 1921, No. 8.

[13] For references to this hypothesis see Bowen, *The Evolution of Igneous Rocks.* Princeton Univ. Press, **1928.**

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## *THE MINIMA OF INDEFINITE QUATERNARY QUADRATIC FORMS*

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Let $f = \sum a_{ik}x_ix_k$ $(a_{ik} = a_{ki})$ be a quadratic form of rank $n$ with real coefficients in $n$ variables $x_1, \ldots, x_n$. The variables assume integer values only, the set 0, 0, . . . excepted. One of the many problems associated with quadratic forms is that of finding the upper bound of $L(f)$, the absolute lower bound of $f$, when $f$ runs over the set of forms which have a given hessian $a = ||a_{ik}||$. We shall consider only real indefinite quaternary forms. For indefinite binary and ternary forms, Markoff* has given two theorems, which are needed in the discussion of quaternary forms. By means of these theorems of Markoff, I have proved the following:

THEOREM. *Let $f$ be an indefinite quaternary quadratic form of hessian $a$. If the signature of $f$ is $-2$ or $+2$ so that $a$ is negative, then*

$$L^4(f) \leqq -\tfrac{4}{7}a, \tag{1}$$

*and, if equality holds, then $f$ is equivalent to the form*

$$\pm f_0 = L(x^2 - y^2 - z^2 - t^2 + xy + xz + xt). \tag{2}$$

*If $f$ is not equivalent to $\pm f_0$, then necessarily*

$$L^4 < -\tfrac{1}{3}a. \tag{3}$$

*If the signature of $f$ is zero so that $a$ is positive, then*

$$L^4 \leqq \tfrac{4}{9}a, \tag{4}$$

*and, if equality holds, then $f$ is equivalent to the form*

$$f_1 = L(x^2 - y^2 - z^2 + t^2 + 2zx + 2xy + xt + yt + zt). \tag{5}$$

*If $f$ is not equivalent to $f_1$, then necessarily*

$$L^4 \leqq \tfrac{4}{15}a. \tag{6}$$

In the present note I give an alternative proof I have discovered of the part of the theorem relating to forms of signature zero, but in this proof the inequality (6) is replaced by the cruder inequality

$$L^8 \leqq \tfrac{16}{135}a^2. \tag{7}$$

A few preliminary remarks applying to forms in $n$ variables will be necessary. The adjoint of $f$ is derived from $f$ by the substitution

$$ay_i = \tfrac{1}{2}\frac{\partial f}{\partial x_i} \equiv \sum a_{ik}x_k,$$

where $a$ is not zero so that the adjoint is

$$g = \sum A_{ik}y_iy_k,$$

where $A_{ik}$ is the cofactor of $a_{ik}$ in $a$.

Let $F$ be obtained from $f$ by the transformation $x_i = \sum X_k l_{ik}$ of determinant $\pm 1$, the $l_{ik}$ being integers. Then the transpose transformation $Y_i = \sum l_{ki}y_k$ carries the adjoint $G$ of $F$ into the adjoint $g$ of $f$. The quadratic form derived from $F$ by putting $s < n$ of the variables $X$ equal to zero is called a section of $f$. If in particular $l_{11} = 1$ and $l_{i1} = 0$ ($i = 2 \ldots, n$) so that the coefficient of $x_1^2$ is unaltered, and we do not put $X_1 = 0$, the section so obtained may be called a section through the axis of $x_1$, or simply a principal section with respect to $x_1$.

Suppose now that $f$ is an indefinite non-nul[†] quaternary quadratic form of signature zero. Every ternary section of $f$ is necessarily indefinite. For suppose the section is obtained by putting $X_4 = 0$. We may write

$$f = b_1 z_1^2 + \ldots + b_4 z_4^2,$$

where $z_i$ is a linear function of $X_i$, $X_{i+1}, \ldots$ Since the signature of $f$ is zero, two of the $b_i$ are positive and two are negative. And it follows at once that the ternary obtained by putting $X_4$ or what is the same thing, $z_4$ equal to zero, is indefinite. Since a form and its adjoint have the same signature, any ternary section of $g$ is also indefinite.

Consider the principal ternary section $F(X_1, X_2, X_3, 0)$ of $f$ under $x_i = \sum l_{ik} X_k$ where $l_{11} = 1$, $l_{i1} = 0$ $(i = 2, 3, 4)$, of determinant $\pm 1$. Its hessian $D$ is the coefficient of $Y_4^2$ in $G$. But the transformation $Y_i = \sum l_{ki} y_k$ carries $G$ into $g$. It follows that $D$ is represented by the ternary $g(0, y_2, y_3, y_4)$ for the integers $y_2, y_3, y_4$ determined from the consistent linear equations obtained by putting $y_1 = Y_1 = Y_2 = Y_3 = 0$ and $Y_4 = \pm 1$.

Conversely, if $D$ is any number properly represented by the ternary $g(0, y_2, \ldots)$, we can find a section of $f$ through the axis of $x_1$ with hessian $D$.

Suppose now that $L$ is not zero and is attained so that it is represented and properly represented by $|f|$. We may therefore take $a_{11} = \pm L$. By Markoff's theorem on indefinite ternary forms, we have

$$|a_{11}|^3 = \tfrac{2}{3}|D| \quad \text{or else} \quad |a_{11}|^3 \leqq \tfrac{2}{5}|D|, \tag{8}$$

for the absolute lower bound of $F(X_1, X_2, X_3, 0)$ is plainly $L$.

Let $M$ be the lower bound of the indefinite ternary $g(0, y_2, y_3, y_4)$ of hessian $a_{11}a^2$. Then

$$M^3 = \tfrac{2}{3}|a_{11}a^2| \quad \text{or} \quad M^3 \leqq \tfrac{2}{5}|a_{11}a^2|, \tag{9}$$

and, if $M$ is not attained, then (9.2) holds with $<$ instead of $<$ or $=$. Since $D$ is any number properly represented by this ternary, we may subject $D$ to the conditions

$$|D|^3 = \tfrac{2}{3}|a_{11}a^2| \quad \text{or else} \quad |D|^3 \leqq \tfrac{2}{5}|a_{11}a^2|. \tag{10}$$

From (8) and (10) we see that $L^3 \leqq \frac{16}{135}\, a^2$, unless both (8.1) and (10.1) hold, in which case $L^4 = \frac{4}{9}\, a$. Employing Markoff's result that an indefinite ternary form for which the cube of the absolute lower bound is equal to two-thirds of the hessian must be equivalent to the appropriate multiple of the form $x^2 - y^2 - z^2 + xy + xz$, which has hessian $3/2$ and minimum unity, we find that the forms of lower bound $L$ which satisfy (8.1) and (10.1) must be equivalent to the form (5), wherein $L^4 = \frac{4}{9}a$.

If $L$ is not attained, rather more argument is required. In this case, if $e$ is any positive number, however small, we can choose $a_{11}$ so that

$L < |a_{11}| < L(1 + e)$. Let $N$ be the absolute lower bound of $F(X_1, X_2, X_3, 0)$. It is easy to see that our previous arguments will yield (1) unless both

$$N^3 = \tfrac{2}{3}|D| \quad \text{and} \quad |D|^3 = \tfrac{2}{3}|a_{11}a^2|$$

for all sufficiently small positive $e$. It is plain that now $L < N$ and that $|a_{11}| = N$ We deduce that $N^4 = 4a|9$ and hence that

$$L^4 < 4a|9 < L^4(1 + e)^4.$$

But clearly this is impossible if $e$ is small enough, since $L$ and $a$ are independent of $e$. Our theorem is therefore proved.

This method fails in the case of forms of signature $\pm 2$, since the ternary sections employed may be definite or indefinite, and the information derived is insufficient to determine the precise upper bound.

The principle of the method is due to Korkine and Zolotareff[9] who applied it to obtain the precise upper bound for the minima of definite forms in four variables from the known upper bound for definite forms in three variables.

We observe finally that for indefinite forms in five or more variable with commensurable coefficients, $L(f)$ must be zero, or, what is here the same thing, $f$ is a nul form. It is very likely true that $L(f)$ must be zero when the coefficients are incommensurable. But this has not yet been proved.

* A. Markoff.[1,2,3] For binary forms see also F. G. Frobenius,[4,5] I. Schur,[6], and R. Remak.[7] Markoff proves his ternary theorem only for forms with commensurable coefficients. It is not difficult however to extend his analysis so as to cover the case of incommensurable coefficients, including therein the case when the lower bound is not necessarily attained. The ternary theorem has been extended by L. E. Dickson.[8]

† If $f$ is nul, our theorem is trivial.

[1] A. Markoff, "Sur les formes quadratiques binaires indefinies," *Math. Ann.*, **15**, 381–409, 1879.

[2] *Ibid.*, **17**, 379–399, 1880.

[3] "Sur les formes quadratiques ternaires indefinies," *Ibid.*, **56**, 233–251, 1903.

[4] G. Frobenius, "Über die Markoffsche Zahlen," *Sitz. Preuss. Akad. Wiss.*, 458–487, 1913.

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[9] A. Korkine and G. Zolotareff, "Sur les formes quadratiques positives quaternaires," *Math. Ann.*, **5**, 581–583, 1872; Korkine, *Coll. Papers*, **1**, St. Petersburg, 285–288, 1911.

# ON THE NUMBER OF CYCLIC SUBGROUPS OF A GROUP

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If $d_1, d_2, \ldots, d_\lambda$ represent all the different positive divisors of the order $g$ of a finite group $G$, and if $\phi(d_i)$ and $a_i$ represent, respectively, the totient of $d_i$ and the number of the cyclic subgroups of order $d_i$, $i = 1, 2, \ldots, \lambda$, contained in $G$, then it results from the fact that two distinct subgroups of the same order cannot have in common any generator of these subgroups and be generated thereby that

$$a_1\phi(d_1) + a_2\phi(d_2) + \ldots + a_\lambda\phi(d_\lambda) = g.$$

It will be assumed that $d_1 = 1$ and that $d_\lambda = g$. Hence it results that $a_1$ is always unity while $a_\lambda$ is either unity or zero. A necessary and sufficient condition that $a_\lambda = 1$ is that $G$ is cyclic, and whenever $a_{\lambda-1}$ then $a_1 = a_2 = \ldots = a_\lambda = 1$. As this case is so elementary it will be assumed in what follows that $a_{1\lambda} = 0$, and it will be seen that whenever this condition is satisfied at least one of the coefficients $a_1, a_2, \ldots, a_{\lambda-1}$ is as large as 3.

When $G$ contains more than one Sylow subgroup of a given order this theorem follows directly from the fact that each of these Sylow subgroups contains at least one cyclic subgroup which is not transformed into itself by a cyclic subgroup of the same order contained in an arbitrary one of the others, since a Sylow subgroup cannot be transformed into itself by another subgroup of the same order. Hence it may be assumed that $G$ is either a prime power group or the direct product of such groups if the non-cyclic group $G$ does not contain at least three cyclic subgroups of the same order. In both cases $G$ must contain a non-cyclic prime power group, and hence it remains only to note that such a group contains at least three cyclic subgroups of some order. When this prime number $p$ is odd it is known that the number of the subgroups of order $p$ contained in $G$ is of the form $1 + kp$, where $k > 0$. When $p = 2$ and $G$ contains only one subgroup of order 2 then the number of its cyclic subgroups of order 4 is known to be of the form $1 + 2k$, where $k > 0$, since $G$ must be dicyclic in this case. Hence we have proved the following theorem: *Every non-cyclic group contains at least three cyclic subgroups of some order.*

1. *Groups containing at least one cyclic subgroup whose order is an arbitrary proper divisor of the order of the group.*

If a non-cyclic group $G$ of order $g$ has the property that it contains at least one cyclic subgroup whose order is an arbitrary proper divisor of $g$, that is, any divisor of $g$ except $g$ itself, then its order cannot be divisible

by more than two distinct prime numbers. To prove this fact we may first note that if $g$ would involve more than two such factors it may be assumed that $q$ is the smallest of them and that $G$ contains a cyclic subgroup $H$ of order $g/q$. It is easy to prove that $H$ must be an invariant subgroup of $G$. This results from the facts that every Sylow subgroup of $G$ except the Sylow subgroups of order $q^n$ must be contained in $H$, and that $q^{n-1}$ of the operators of each of the latter Sylow subgroups must also appear therein according to well-known theorems. Since an operator $s$ of order $q^n$ must appear in cyclic groups whose separate orders are the product of $q^n$ and the order of each of the other Sylow subgroups it results that $s$ must be commutative with every operator of $H$. This is impossible since $G$ is non-cyclic and hence it has been proved that $g$ cannot be divisible by more than two distinct prime numbers.

It may now be assumed that $g = p^m q^n$ and that the invariant subgroup $H$ is of order $p^m q^{n-1}$. Since the group of isomorphisms of the cyclic group of order $p^m$ is cyclic and $G$ is non-abelian it results that $p - 1$ is divisible by $q$. If $m > 1$, then $G$, therefore, cannot contain a cyclic subgroup of order $p^{m-1}q^n$. Hence $m = 1$ while $n$ can have any arbitrary value greater than 0. Moreover, the group $G$ is completely determined by this value of $n$ whenever $p$ and $q$ are given prime numbers. Hence the following theorem has been established: *If a non-cyclic group $G$ of order $g$ has the property that it involves at least one cyclic subgroup whose order is an arbitrary proper divisor of $g$, then $g$ is divisible by at most two distinct prime numbers $p$ and $q$, and when $g$ is divisible by both of these numbers and $p > q$ then $p - 1$ is divisible by $q$ and $g = pq^n$. Moreover, there is one and only one such group for every positive value of $n$ and it contains only cyclic proper subgroups. Every such group contains $p$ such subgroups of order $q^n$ but only one such subgroup of each other order.*

In order to complete the determination of all the non-cyclic groups which have the property that each of them contains at least one cyclic subgroup whose order is an arbitrary proper divisor of the order of the group it remains only to consider the groups of order $p^m$, $p$ being a prime number, which have this property. All of these groups are known since all the groups of order $p^m$ which contain a cyclic subgroup of order $p^{m-1}$ have been determined. Hence there is one and only one such abelian group for every value of $m > 1$, and there is also one and only one such non-abelian group which is conformal with this abelian group whenever $m > 3$. When $p$ is odd the latter group exists also when $m = 3$ and there is no other group which satisfies these conditions. When $p = 2$ and $m = 3$ the octic and the quaternion group satisfy these conditions, while when $p = 2$ and $m > 3$ there are five groups of order $2^m$ which satisfy these conditions. By combining these known results with the theorem closing the preceding paragraph we therefore obtain all the non-

cyclic groups which satisfy the condition that each group contains at least one cyclic subgroup whose order is an arbitrary proper divisor of the order of the group.

2. *Groups containing at most three cyclic subgroups of the same order.* It was noted above that every non-cyclic group contains at least one set of cyclic subgroups of the same order which includes as many as three such subgroups. We proceed to consider all those non-cyclic groups which contain no more than three cyclic subgroups of the same order. Since every non-cyclic group of order $p^m$, $p$ being any odd prime number, contains at least $1 + p$ subgroups of order $p$ it results that every Sylow subgroup of odd prime power order which appears in such a group $G$ of order $g$ must be cyclic. If $g = 2^m$ and contains more than one cyclic subgroup of order 2, $\alpha > 2$, it must contain an even number of such subgroups and hence this number must be 2 in the present case. If $G$ contains exactly three cyclic groups of order 4 it is known to be either the quaternion group or the group of order 16 obtained by extending the cyclic group of order 8 by operators which transform into their third power each operator of this cyclic group. As the latter contains five subgroups of order 2 it does not satisfy the conditions under consideration and the quaternion group is therefore the only group of order $2^m$ which satisfies these conditions and contains exactly three cyclic subgroups of order 4. *Hence the quaternion group is the only group of order $2^m$ which satisfies the two conditions that it contains no more than three cyclic subgroups of any order and that it contains exactly three cyclic subgroups of order 4.*

In order to complete the determination of all the non-cyclic groups of order $2^m$, which contain at most three cyclic subgroups of the same order, it remains only to consider those which have three subgroups of order 2 and two cyclic subgroups of each of the orders 4, 8, . . ., $2^{m-1}$. In fact, since $a_\lambda = 0$ and $\phi(2^m) = 2^{m-1}$ each of the literal coefficients in the equation

$$\phi(1) + 3\phi(2) + a_3(d_3) + \ldots + a_{\lambda-1}\phi(d_{\lambda-1}) = 2^m$$

must be equal to 2. Hence there is one and only one abelian, and one and only one non-abelian group of order $2^m$, $m > 3$, which satisfies these conditions. These two infinite systems of conformal groups together with the non-cyclic group of order 4, the quaternion group, and the abelian group of order 8 and of type (2, 1) are therefore the only non-cyclic groups of order $2^m$ which satisfy the condition that each of them contains no set of more than three cyclic subgroups of the same order.

If $g$ is divisible by more than one prime number it may be the direct product of any one of the groups just determined and an arbitrary cyclic group of odd order or it may contain more than one Sylow subgroup of

order $2^m$. In the latter case each of its Sylow subgroups must be cyclic and $G$ must involve an invariant cyclic subgroup whose order is the direct product of the cyclic group of order $3.2^{m-1}$ and an arbitrary cyclic group whose order is prime to 6. Moreover, any such direct product can be extended by an operator of order $2^m$, which transforms the operators of order 3 in this cyclic group into their inverses but is commutative with each of the other operators contained therein so as to obtain a group which has three cyclic subgroups, when the order of such a subgroup is $2^m$, into any divisor of the order of the group which is prime to 6, but only one such subgroup when its order is not divisible by $2^m$. Hence the following theorem: *If a group contains no more than three cyclic subgroups of the same order and is not a prime power group nor the direct product of such groups it can be constructed by extending the group which is the direct product of the cyclic group of order $3.2^{m-1}$ and any cyclic group whose order is prime to 6 by means of an operator of order $2^m$ which has its square in this direct product and transforms into their inverses the operators of order 3 contained therein but is commutative with all its other operators.*

[1] Miller, Blichfeldt, Dickson, *Finite Groups*, p. 131, **1916.**

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## *ON NEW INTEGRAL ADDITION THEOREMS FOR BESSEL FUNCTIONS*[1]

BY HENRY P. THIELMAN

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Communicated August 5, 1929

This paper contains some of the main results obtained by the author, which together with their derivations are to be published elsewhere. In obtaining these results use has been made of the theory of functional composition as developed by Vito Volterra[2] and Joseph Pérès.[3] It must be said that Hadamard[4] has derived certain integral addition theorems for Bessel Functions. His results are, however, particular cases of a more general theorem stated here.

THEOREM. *Two Bessel functions of any orders $\alpha > -1$, $\beta > -1$ have the additive properties expressed by the following equations:*

$$\int_x^y [a(x-t)]^{\frac{\alpha}{2}} J_\alpha[2\sqrt{a(x-t)}]\,[b(t-y)]^{\frac{\beta}{2}} J_\beta[2\sqrt{b(t-y)}]\,dt =$$

$$\frac{a^\alpha b^\beta [(a+b)(x-y)]^{\frac{\alpha+\beta+1}{2}}}{(a+b)^{\alpha+\beta+1}} J_{\alpha+\beta+1}[2\sqrt{(a+b)(x-y)}] \qquad (1)$$

$$\int_x^y [a(x-t)]^{\frac{\alpha}{2}} J_\alpha[2\sqrt{a(x-t)}][b(t-y)]^{-\frac{1}{2}} J_1[2\sqrt{b(t-y)}]dt =$$

$$\frac{a^\alpha[(a+b)(x-y)]^{\frac{\alpha}{2}}}{b(a+b)^\alpha} J_\alpha[2\sqrt{(a+b)(x-y)}] -$$

$$\frac{a(x-y)]^{\frac{\alpha}{2}}}{b} J_\alpha[2\sqrt{a(x-y)}] \quad (2)$$

$$\int_x^y [a(x-t)^{-\frac{1}{2}} J_1[2\sqrt{a(x-t)}][b(t-y)]^{\frac{\beta}{2}} J_\beta[2\sqrt{b(t-y)}]dt$$

$$= \frac{b^\beta[(a+b)(x-y)]^{\frac{\beta}{2}}}{a(a+b)^\beta} J_\beta[2\sqrt{(a+b)(x-y)}]$$

$$- \frac{[b(x-y)]^{\frac{\beta}{2}}}{a} J_\beta[2\sqrt{b(x-y)}] \quad (3)$$

$$\int_x^y [a(x-t)]^{-\frac{1}{2}} J_1[2\sqrt{a(x-t)}][b(t-y)]^{-\frac{1}{2}} J_1[2\sqrt{b(t-y)}]dt$$

$$= \frac{(a+b)J_1[2\sqrt{(a+b)(x-y)}]}{ab[(a+b)(x-y)]^{\frac{1}{2}}}$$

$$- \frac{J_1[2\sqrt{a(x-y)}]}{b[a(x-y)]^{\frac{1}{2}}} - \frac{J_1[2\sqrt{b(x-y)}]}{a[b(x-y)]^{\frac{1}{2}}} \quad (4)$$

To obtain Hadamard's result from this theorem we proceed as follows:

We write

$$j_p(\overline{X}) = (-\overline{X})^{\frac{p}{2}} J_p[2\sqrt{-\overline{X}}] \quad (5)$$

and note that

$$d[j_q(bt)] = b j_{q-1}(bt)dt \qquad q > 0. \quad (6)$$

If in (1) we interchange $a$ and $b$, and set $\alpha = q - 1$, $\beta = p$, $x = 0$, $y = 1$, this equation can be written, by means of (5) and (6), in the form

$$\int_{t=0}^1 j_p[a(1-t)]d[j_q(bt)] = \frac{a^p b^q}{(a+b)^{p+q}} j_{p+q}(a+b),$$

which is the general theorem of Hadamard.

If in (3) we interchange $a$ and $b$, and set $\beta = p$, $x = o$, $y = 1$, then noting that

$$d[j_o(bt)] = \frac{j_1(bt)}{b}\, dt,$$

we obtain the equation

$$\int_{t=o}^{1} j_p[a(1-t)]d[j_o(bt)] = \frac{a^p j_p(a+b)}{(a+b)^p} - j_p(a),$$

which is the exceptional case in Hadamard's general theorem.

We thus see that *Hadamard's result corresponds to particular cases of equation* (1) *and* (3), while there is nothing in his work which might correspond to equation (4).

By means of a new theory of composition on functions in $2n$ variables ($n = 1, 2, 3, \ldots$) the author has derived integral addition theorems for hypergeometric series of a certain generalized type, which correspond to equations (1) to (4) of this paper.

[1] The writing of this paper was suggested by Professor A. D. Michal.

[2] Vito Volterra, *Lecons sur les fonctions de lignes*, Paris (1913). *The Theoy of Permutable Functions*, Princeton University Press (1915).

[3] Vito Volterra et Joseph Pérès, "Leçons sur la composition et les fonctions permutable."

[4] Hadamard, "Sur un probleme mixte aux derivées partielles," *Bulletin de la Société Mathématique de France*, tome 31 (1903), p. 220.

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## *DWARF, A NEW MENDELIAN RECESSIVE CHARACTER OF THE HOUSE MOUSE*

BY GEORGE D. SNELL

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Communicated July 22, 1922

During the course of the past winter a new recessive mendelian character, dwarf, was found among the mouse stocks of the writer at the Bussey Institution. This is the second case of hereditary dwarfism to appear in rodents. The first was found by Sollas* who has reported a strain of guinea-pigs in which $^1/_4$ of the young (25 out of 99) from certain matings were undersize and malformed at birth. Most of these dwarf guinea-pigs died very early, and the few that lived were sterile and did not attain more than about one half normal size. The shape of the skull and various bones of the body was also altered.

In the case of the dwarf mice, mature individuals are only about one fourth the weight of their normal brothers and sisters, scarcely bigger in fact than an ordinary mouse 16 or 17 days old. It is not until the 14th day, however, that their reduced size begins to manifest itself. Up to this time they grow as rapidly as their unaffected sibs, though they can usually be identified on the 12th or 13th day by their shorter noses and

tails. After 14 days they grow scarcely at all, though aside from permanent shortness of their noses, most parts of the body especially ears and tail, develop enough to make the proportions of the animal as a whole those of an adult. The opening of the eyes is delayed by 2 or more days beyond its usual time of occurrence at 14 days.

Despite their greatly reduced size, the dwarf mice are fairly healthy. All that have so far appeared (and not intentionally been killed) are still alive, the oldest being now 5 months of age. In vigor they are somewhat sub-normal, showing very little tendency to run about and never trying to jump out of the jar in which they are placed during examination. Both males and females, so far as can be judged from tests made to date, are entirely sterile.

The character was derived from a strain of black silver mice very kindly given to the writer by Dr. L. C. Dunn, who obtained them from Wm. Turton, a fancier of Ilkeston, England. They originally appeared in the $F_2$ of crosses of a silver male, *S*13, with two different pink-eyed females and also among the offspring of a silver male and female mated together. Some of the normal $F_2$s from male *S*13 have now been proved to be heterozygous for the character, as a number of dwarf mice have appeared in $F_3$, and in litters from a backcross of $F_2$ to $F_1$. Matings of heterozygotes have so far yielded 103 normals to 34 dwarfs, a very close approximation to the expected 3:1 ratio. Owing to the sterility of the dwarfs, matings of homozygous recessives with heterozygotes and *inter se* have not been possible, but the clear-cut nature of the character, its appearance in a 3:1 ratio in $F_2$, and the fact that it has now been carried through two generations in the heterozygous condition since its first appearance, clearly establish it as a recessive unit factor.

Linkage tests are now in progress and will be reported in detail later, but it is already clear that dwarf is not sex-linked and probably not linked with pink-eye or dilution.

It is planned to undertake a physiological study of the dwarf mice as it seems likely that they will furnish excellent experimental material for various problems in connection with growth.

* Sollas, I. B. J., "Inheritance of Colour and of Supernumerary Mammæ in Guinea-Pigs, with a Note on the Occurrence of a Dwarf Form," *Reports Evol. Com. Royal Soc.*, **5**, 51–79 (1909).

# CRITERIA OF MALE AND FEMALE IN BREAD MOULDS (MUCORS)[1]

BY SOPHIA SATINA AND A. F. BLAKESLEE

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Communicated August 10, 1929

The Mucors, commonly called bread moulds, are a group of fungi apparently simple in structure and in their methods of reproduction. All are able to multiply rapidly, perhaps indefinitely, by means of non-sexual spores. We have still in cultivation, for example, the sexual races of the common Rhizopus which were isolated in 1904. A few species are hermaphroditic (homothallic) and produce sexual spores (zygospores) through the interaction of branches from the same individual. The great majority, however, are dioecious (heterothallic) and require for sexual reproduction the interaction of individuals of the two opposite sexes provisionally designated as (+) and (−). Which of these two sexes is male and which is female is the problem of our present discussion.

The process of zygospore formation in dioecious species can be illustrated by figure 1, *a-e*. Two filaments of opposite sex (*a*) produce, at the point

FIGURE 1

of contact, swellings which enlarge (*b*), and from which cross walls cut off gametangia (*c*) which are morphologically indistinguishable. By dissolution of the intervening double wall, the contents of the gametangia are brought in contact (*d*) and the fusion cell thus formed develops into a mature thick-walled zygospore (*e*) which apparently functions as a resting spore. The cells of Mucors are multinucleate, and the filaments are usually without cross walls except at the formation of the reproductive bodies. Since the uniting sex cells contain more than a single nucleus they are called gametangia instead of gametes.

The nuclei are minute and their behavior is difficult to follow. Probably for this reason, although there has been considerable cytological work done on Mucors, there is no general agreement regarding the cytological happenings during sexual reproduction. Few[2] have ventured to suggest even the presence of chromosomes. It is unreasonable, therefore, to expect much aid from a study of the chromosomes in determining which of the two sexes in Mucors corresponds to the male and which to the female of higher types of plants.

Tests with over 2000 races included in thirty-four or more species and twelve genera furnish ample evidence[3] that in the dioecious Mucors we have two and only two sexes present comparable to those in higher forms. Races of given species were grown in pairs under conditions suitable to zygospore formation and the reactions recorded. Between 10,000 and 20,000 such intraspecific combinations have been made without evidence for sex intergrades. The supposed examples of sex intergrades in the Mucors have been based upon relatively meager data and, as we have shown,[4] were probably wrongly interpreted. A given race shows itself to be either (+), (−) or fails to show any sexual reaction and is classed as a "neutral." Such neutral races are perhaps actually (+) or (−) but not of sufficient sexual activity to take part in zygospore formation with the races of the opposite sex with which they have been tested. Various grades of sexual vigor are apparent in the different races tested within a single species and some would have been classed as neutrals if they had not been tested with a particular race of the opposite sex with which they gave a scanty production of zygospores. We have found no evidence for "relative sexuality" in the dioecious Mucors such as Hartmann[5] has described in Ectocarpus and believes exists in a wide range of forms.

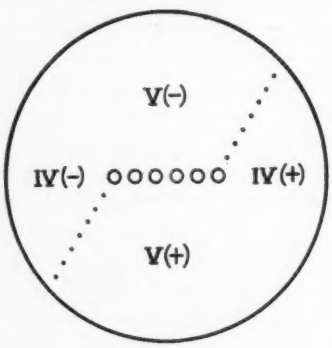

FIGURE 2

Not only are there only two sexes within a given species but the same two sexes are present throughout all the species tested as shown by the "imperfect hybridization" reaction. Figure 2 is a diagram of a culture in which zygospores are represented by circles at the line of contact between (+) and (−) races of species V. In the same culture were planted the opposite sexes of another species IV. The dotted lines represent the imperfect sexual reactions which take place when opposite sexes belonging to two different species come in contact. Such imperfect reactions may be so abundant as to be visible as a white line. The reactions resemble early arrested stages in zygospore formation and never reach a more advanced stage than the formation of gametangia shown in figure 1*c*.

Imperfect hybridization reactions have been employed in determining the sex of unmated races[6] and have led to the conclusion that there is something fundamental in common to the same sex throughout all the species in the Mucors. Imperfect reactions have also shown that the

same (+) and (−) sexes exist in the single individuals of hermaphroditic species.[7]

Although no constant morphological differences have been observed in the uniting gametangia of dioecious species nor in those of several hermaphroditic species, there are certain species of the latter in which there is a striking and constant difference in gametangia size, connected with differences in the hyphae which bear them. Since in practically all forms in which there is a size difference between gametes (the larger is

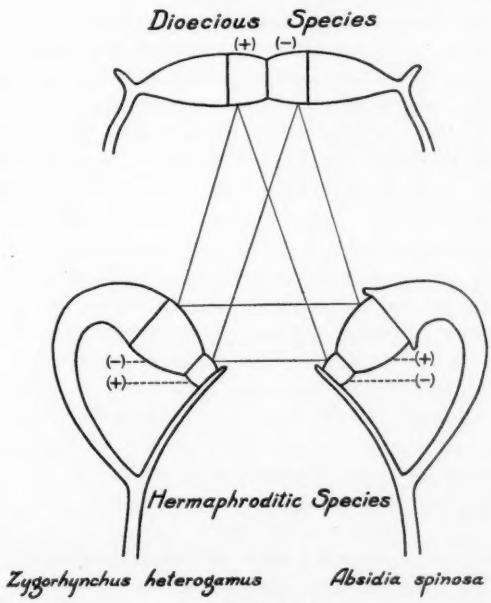


FIGURE 3

the female) it was thought possible by imperfect reactions to determine which sex of dioecious Mucors showed an imperfect reaction with the larger gametangia of these heterogamic hermaphrodites and thus to be able to say which of the (+) and (−) sexes was male and which female. Earlier investigations showed that the (+) race reacted with the smaller gametangium of three species of heterogamic hermaphrodites and the (−) race reacted with the larger gametangium of one of the three. These reactions would seem to warrant one in calling the (+) sex female and the (−) male. A preliminary test of a fourth heterogamic hermaphrodite, however, seemed to give somewhat different reactions with (+) and (−) testers of dioecious species and rendered it inadvisable to draw definite

conclusions as yet as to the homologies of sexes in Mucors and higher forms. The matter seemed worthy of a more detailed study, the results of which are summarized in the succeeding paragraphs.

Figure 3 presents diagrams of the sexual reactions between three types. The one above is a dioecious species used as a standard tester and its gametangia are labeled (+) and (−). The two types below, Absidia spinosa on the right, Zygorhynchus heterogamus on the left, are hermaphrodites with unequal gametangia, the larger in each case borne on the termination of an enlarged branch.

The connecting lines in the diagram show the imperfect sexual reactions which have been observed. Thus (+) races of the dioecious species give reactions with the small gametangium of Absidia spinosa showing that the smaller gametangium of this species is (−) while the (−) race reacts with the larger gametangium showing that the latter is (+). A number of other heterogamic hermaphrodites (Dicranophora, Zygorhynchus Moelleri, Z. Vuillemini, etc.) give imperfect sexual reactions like those of Absidia spinosa. Zygorhynchus heterogamus, however, of which we have tested 4 races behaves differently from any other species investigated. In this species the smaller gametangium from its reactions must be considered (+) and the larger (−), a condition exactly the reverse of that found in Absidia spinosa. Imperfect sexual reactions occur between two hermaphrodites. When Absidia spinosa is grown with Zygorhynchus heterogamus, the large gametangium of the one species reacts with the large gametangium of the other while the small gametangia of the two species react similarly inter se. The imperfect sexual reactions between these two hermaphrodites are such as might be expected from the nature of their gametangia as determined by their reactions with (+) and (−) races of dioecious species.

If, in the evolution of these forms, the heterogamic condition has been derived from isogamy, it is obvious that in one species the (+) has developed into the small gametangium while in others the (+) has developed into the large gametangium. It is as if in some species the eggs were male and the sperms female sex cells. Such a condition, so far as we are aware, is without parallel. It raises the question whether in groups, within which the sexual interactions have not been so thoroughly studied, it is safe to homologize the sexes on the basis of size of conjugating gametes. In one of the flagellates, Mastigella vitrea, according to Wilson,[8] Goldschmidt found that the male gamete is non-motile while the female gamete is flagellated and in Monocystis sp., one of the Gregarines, according to Hartmann,[9] Naville found that the male are larger than the female gametes, but the differences shown in the figures given are at best slight.

In no case in the literature, however, have we found record of the male cell being constantly so markedly superior in size to the female as is the

case with at least one of our heterogamic hermaphroditic Mucors. This is true whether the (+) is female and the (−) male as the reactions with Absidia spinosa would suggest or vice versa as the reactions with Zygorhynchus heterogamus alone might indicate. It would seem that in the Mucors the terms (+) and (−) are labels of something more fundamental than the terms male and female if these latter are defined by size differences in the conjugating cells.

In our discussion we have applied the sex terms (+) and (−) to gametangia. There has been a proper objection to applying the terms male and female to sperms and eggs in flies and mammals without regard to their chromosomal constitution, since half of the sperms have the same sex chromosomes as the eggs. It appears that the reactions of these gametes is not determined by their chromosomal constitution alone. Similarly the reactions of what has been convenient to call (+) and (−) gametangia in Mucors may not be due to differences in chromosomal content. They may differ in somewhat the same way as do sperms and eggs.

It has been seen that there is no constant size difference between the gametangia in dioecious Mucors nor constant vegetative characters by means of which it is possible to distinguish the two sexes. The attempt to determine which is male and which female by imperfect sexual reactions with heterogamic hermaphrodites has been unsuccessful.

A rather extensive series of qualitative and quantitative tests indicates that the (+) races of Mucors react biochemically in a similar manner to the females of higher plants and the (−) races like males.[10, 11, 12, 13] The evidence from these tests suggests that our (+) sex is female and our (−) sex male and is in line with the evidence from imperfect hybridization reactions with all except one species of the heterogamic hermaphrodites. Until further evidence is available, it will not be possible to be certain regarding the homologies of the two sexes in Mucors and higher forms. As a matter of convenience, however, we may designate the (+) and (−) races as tentatively female and male.

The detailed data upon which the present summary is based are being published elsewhere.

[1] The investigation was carried on under joint support of the Carnegie Institution of Washington and Mrs. Walter S. Franklin, Mrs. Walter B. James and Walter Jennings, to whom the authors gratefully acknowledge their indebtedness.

[2] Burgeff, H., *Flora*, **108**, 353–448, 1915.

[3] Blakeslee, A. F., Cartledge, J. L., Welch, D. S., and Bergner, A. D., *Bot. Gaz.*, **84**, 27–50, 1927.

[4] Blakeslee, A. F., Cartledge, J. L., and Welch, D. S., *Ibid.*, **72**, 185–219, 1921.

[5] Hartmann, M., *Biol. Zentralbl.*, **45**, 449–467, 1925.

[6] Blakeslee, A. F., and Cartledge, J. L., *Bot. Gaz.*, **84**, 51–57, 1927.

[7] Blakeslee, A. F., *Biol. Bull.*, **25**, 87–102, 1915.

[8] Wilson, E. B., *The Cell in Development and Heredity*, 3rd ed., Macmillan Co., p. 592, 1925.

[9] Hartmann, M., Verteilung, Bestimmung und Vererbung des Geschlecht bei den Protisten und Thallophyten, *Handbuch. Vererbung.*, B2, Lief 9, Gebrüder Borntraeger, Chap. 2, p. 74, 1929.

[10] Satina, S., and Blakeslee, A. F., These PROCEEDINGS, **11**, 528–534, 1925.

[11] Satina, S., and Blakeslee, A. F., *Ibid.*, **12**, 191–202, 1926.

[12] Satina, S., and Blakeslee, A. F., *Ibid.*, **13**, 115–122, 1927.

[13] Satina, S., and Blakeslee, A. F., *Ibid.*, **14**, 308–316, 1928.

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## *INFLUENCE OF ALUMINIUM ON MORTAR STRENGTH*

BY H. W. LEAVITT, J. W. GOWEN AND L. C. JENNESS

MAINE TECHNOLOGY EXPERIMENT STATION, NO. 8

Communicated July 19, 1929

The writers have for some years been analyzing the variation in the strength developed by mortars made from native sands and common commercial cements. This variation in actual test condition lies between 100 and 600 pounds per square inch in tension and 2500 to 9000 pounds in compression. Among the constituents shown to account for part of this variation in strength is the amount of native iron* found in the sand, a correlation of 0.38 ± 0.03 existing between the content of this native iron and strength. In this paper another sand constituent, aluminium, is studied and its relation to the strength developed by the mortar containing it.

Table 1 shows that there is a consistent increase in the tensile strength developed by mortar on the 28-day test as the content of aluminium found in the native sand increases. This increase amounts to more than 100 pounds over the whole range of variation in the native sands' aluminium content.

TABLE 1

AVERAGE 28-DAY TENSILE STRENGTH OF MORTARS IN RELATION TO THE VARIATION IN ALUMINIUM CONTENT OF THE NATIVE SANDS

| ALUMINIUM CONTENT, % | NUMBER OF SANDS | MEAN MORTAR STRENGTH, 1: 3 MIX |
|---|---|---|
| 0.25–0.50 | 17 | 298 |
| 0.50–0.75 | 28 | 339 |
| 0.75–1.00 | 15 | 333 |
| 1.00–1.25 | 17 | 379 |
| 1.25–1.50 | 15 | 385 |
| 1.50–1.75 | 11 | 399 |
| 1.75–3.75 | 14 | 418 |

The amount of variation which exists for any one class and the degree of correlation which exists between the aluminium content and strength

may be seen in tables 2 and 3. Table 2 represents the 28-day tension results and table 3 the 7-day tension results.

Tables 2 and 3 show that as the amount of aluminium in the sand increases the breaking strength increases. The straight lines on the tables show the general trend in the relationship. The correlation coefficients for aluminium and strength are: 7-day, 0.36 ± 0.05, and 28-day, 0.41 ± 0.05. The correlation is, therefore, significant. It will be further noticed that within any given class of aluminium per cents, breaking strengths still have a fairly wide variation. Thus while the aluminium content significantly affects strength it is clearly not the only limiting variable. In fact, we already know another chemical constituent which also plays a part, namely, iron. The part which this iron content plays in relation to the aluminium content will be analyzed in the succeeding paper.

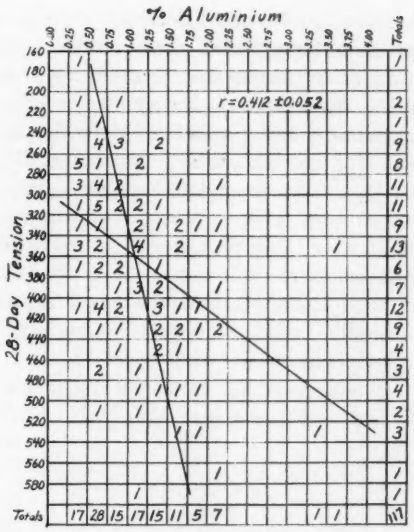


TABLE NO. 2

Relation between aluminium content and 28-day strength.

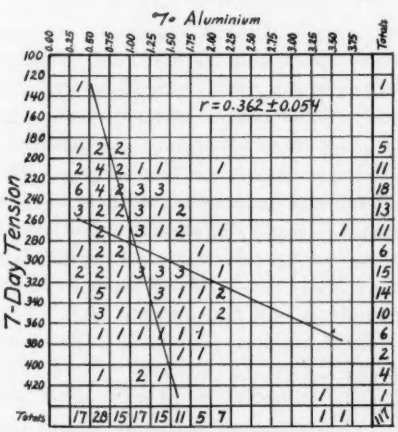


TABLE NO. 3

Relation between aluminium content and 7-day tensile strength.

The amount of variation in the strength for which the variation in aluminium content is responsible is shown by the correlation coefficients to be about 8% of the total variation in mortar strength. The fact that the correlation coefficients are approximately the same for the 7-day and 28-day tests shows that the aluminium content continues to be equally effective in raising or lowering the tensile strength throughout this duration of life of the mortar.

Aluminium content does not have the same marked effect on the compression strength of these mortars. In fact, the correlation between aluminium content and compression strength for these 117 sands is only 0.115 ± 0.062, scarcely significant. Thus again we have called to our attention a fact emphasized elsewhere in our papers, i.e., that the tensile test for mortar strength measures different attributes of the mortar strength than the compression strength.

*Summary.*—The evidence presented clearly indicates the importance of another chemical element of native sand in affecting mortar strength. Aluminium in these native sands affects 7-day and 28-day tensile strength in such a manner that the larger its amount the greater is the tensile strength. Aluminium does not materially affect the strength of the test cylinders in compression.

* "Influence of Iron Content on Mortar Strength," by H. Walter Leavitt and John W. Gowen, *Proc. Nat. Acad. Sci.*, **13**, No. 4, pp. 263–265, April, 1927.

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## *ON THE JOINT INFLUENCE OF IRON AND ALUMINIUM IN NATIVE SANDS ON MORTAR STRENGTH*

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In the preceding papers the influence of iron and aluminium content of native sands on the strength of these sands in mortar has been analyzed separately. In this paper the joint influence of these elements on strength will be shown in its true perspective. Table 1 shows the relation of the iron content to the aluminium content of these 117 sands. Measured in terms of correlation this relation is 0.384 ± 0.054. The effect of the iron content on mortar strength has been indicated elsewhere[1] to be 0.377 ± 0.034 for the 28-day period. A rapid digestion technique was used for the determination of the iron in the 284 sands involved. For the 117 sands here utilized the relation was 0.323 ± 0.055 where the iron content was determined by a digestion test of 5 hours in hot HCl. The results are essentially the same. The aluminium content in relation to strength is shown in the preceding paper to be 0.412 ± 0.052.

From these three possible correlations the influence of any one of the elements on another with the third constant may be found. Thus the correlation for aluminium and strength with the amount of iron constant is 0.330 ± 0.055, for aluminium and iron for strength constant is 0.291 ± 0.051, and for iron and strength for aluminium constant is 0.196 ± 0.058.

The most important of these elements in determining the strength of the 117 native sands is the aluminium content. Iron, however, still retains an important influence even with the aluminium constant.

The joint influence of the two elements, iron and aluminium, is measured by the total correlation coefficient, $r$. This total correlation is equal to $+0.538$. The joint influence of iron and aluminium thus accounts for about 16% of the variation in mortar strength.

The influence of the two elements may be expressed in slightly different form, the equation for the probable strength of the mortar determined from the aluminium and the iron. This equation is:

$$\text{Mortar strength} = 20\,\text{Aluminium}\% + 43\ \text{Iron}\ \% + 272.$$

The equation for strength shows that the two variables both in conjunction with each other and separately play a part in the strength of the mortar. The results therefore point to the conclusion that different chemical constituents of the native sands, aluminium and iron, affect tensile strength in mortars.

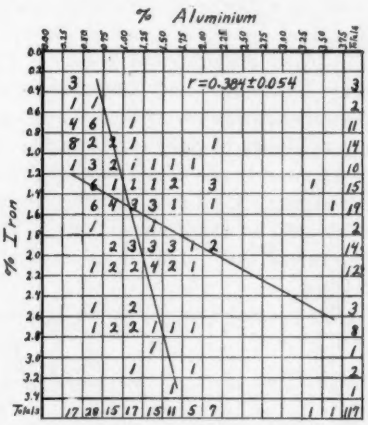


TABLE NO. 1

Relation between the content of iron and aluminium in native sands.

*Summary.*—The results herein presented furnish proof of the fact that iron and aluminium jointly and separately materially influence the strength developed by mortars made from native Maine sands. This conclusion we feel justified in extending to the more general type, the chemical condition of the sand used in cement mortars materially influences the strength of these mortars when hardened. Proof is thus furnished of the chemical interaction of the sand and the cement.

[1] "Influence of Iron Content on Mortar Strength," by H. Walter Leavitt and John W. Gowen, *Proc. Nat. Acad. Sci.*, **13**, No. 4, pp. 263–265, April, 1927.

# PLANETARY MOTION IN A RETARDED NEWTONIAN POTENTIAL FIELD

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The problem of the motion of a planet within a solar system which is itself in uniform motion with respect to an "absolute" space has been discussed from the time of Laplace up to shortly after the advent of Einstein's gravitational theory. The latest work seems to have been done by Lodge[1] and Eddington,[1] who conclude that the pre-relativity discrepancies between theory and observation are not explicable in terms of variability of mass with velocity of the planet.

Apparently no one has thought of applying to gravitation the idea corresponding to that of effective charge which Lienard[2] and Wiechert[3] developed in electromagnetism. The application is simple; in order to determine the potential of a moving gravitating mass we proceed as follows:

The potential at any point 0 is given by the expression

$$\Phi = k \int\int\int \frac{\rho dV_e}{r_e},$$

integrated over the boundaries of the body, $dV_e$ and $r_e$ being the "effective" volume and radius; the first is the element of volume in a fixed reference system within which each point of the moving element was located at the time when it gave rise to the potential existing at 0 at the slightly later time when the distance from the moving element to 0 is $r$, while $r_e$ is the distance of the center of $dV_e$ from 0. Hence in rectangular fixed axes with $x$-axis in the direction of motion of the mass, if $x$, $y$, $z$, be the instantaneous coördinates of a point of any element of the mass, and $x_e$, $y_e$, $z_e$ the effective coördinates, then

$$\begin{aligned} x_e &= x - vt \\ y_e &= y \\ z_e &= z \end{aligned}$$

where $v$ is the velocity of the body and $t$ is the time of propagation of gravitation from the point to 0. If the coördinates of 0 are $x'$, $y'$, $z'$, $r_e^2 = c^2t^2$ (where $c$ is velocity of gravitation)

$$\begin{aligned} &= (x' - x_e)^2 + (y' - y_e)^2 + (z' - z_e)^2 \\ &= (x' - x)^2 + (y' - y)^2 + (z' - z)^2 + 2vt(x' - x) + v^2t^2. \end{aligned}$$

Or $$(c^2 - v^2)t^2 - 2v(x' - x)t - r^2 = 0,$$

$$\therefore\ l = \frac{1}{1-\beta^2}\left\{\frac{v}{c^2}(x'-x) + \frac{r}{c}\left[1 - \frac{\beta^2}{2}\left(1 - \frac{(x'-x)^2}{r^2}\right)\right]\right\}$$

where $$\beta = \frac{v}{c}.$$

$\therefore\ x_e = x - \beta r - \beta^2(x'-x)$ (if $\beta^3$ and higher powers are neglected) and

$$dx_e = \frac{\partial x_e}{\partial x}dx + \frac{\partial x_e}{\partial r}\frac{\partial r}{\partial x}dx = (1 + \beta\cos\theta + \beta^2)dx$$

where $\theta$ is angle between $x$-axis and $r_e$.

$$\therefore\ dV_e = dy_e\, dz_e\, dx_e = (1 + \beta\cos\theta + \beta^2)dV.$$

Also $$r_e = ct = r[1 + \beta\cos\theta + \beta^2(1 + \cos^2\theta)]$$

$$\therefore\ \Phi = k\iiint \frac{\rho(1 + \beta\cos\theta + \beta^2)dV}{r\left[1 + \beta\cos\theta + \frac{\beta^2}{2}(1 + \cos^2\theta)\right]}$$

$$= k\iiint \frac{\rho}{r}\left(1 + \frac{\beta^2}{2}\sin^2\theta\right)dV,$$

if powers of $\beta$ above the second are ignored, as they will be henceforth without mention.

Two distinct cases will be dealt with in determining the orbits; in the first it will be assumed that mass of planet is simply a constant independent of velocity and of direction of acceleration, while in the second the mass will be assumed to correspond to that of the Lorentz electron. In both cases the central mass can be treated as a homogeneous sphere, since only small corrections are being computed; hence, we may write for the present purpose

$$\Phi = \frac{\mu}{r}\left(1 + \frac{\beta^2}{2}\sin^2\theta\right)$$

where $\mu$ is a constant.

*Case I.*—Mass of planet constant.

Here we can apply Lagrange's equations in usual form

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_\alpha}\right) - \frac{\partial T}{\partial q_\alpha} = Q_\alpha. \qquad (1.1)$$

Choosing polar coördinates $r$, $\theta$ in plane of orbit, and using $\beta$ for ratio of component of "absolute" velocity of the sun in that plane to velocity of gravitation, we have, since $T = \frac{m}{2}(\dot{r}^2 + r^2\dot{\theta}^2)$

$$\frac{\partial T}{\partial \theta} = m\dot{\theta}r^2 \quad , \quad \frac{\partial T}{\partial \theta} = 0$$

$$\frac{\partial T}{\partial r} = m\dot{r} \quad , \quad \frac{\partial T}{\partial r} = mr\dot{\theta}^2$$

$$Q_\theta = \frac{\partial \Phi}{\partial \theta} = \frac{\mu\beta^2}{2r} \sin 2\theta \tag{1.2}$$

$$Q_r = \frac{\partial \Phi}{\partial r} = -\frac{\mu}{r^2}\left(1 + \frac{\beta^2}{2}\sin^2\theta\right). \tag{1.3}$$

Substituting these values in (1.1) we get the simultaneous equations

$$\frac{d}{dt}(r^2\dot{\theta}) = \frac{\mu\beta^2}{2}\frac{\sin 2\theta}{r} \text{ and} \tag{1.4}$$

$$\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2 = -\frac{\mu}{r^2}\left(1 + \frac{\beta^2}{2}\sin^2\theta\right). \tag{1.5}$$

Multiplying (1.4) by $2r^2\dot{\theta}$ we get

$$\frac{d}{dt}(r^2\dot{\theta})^2 = \mu\beta^2 r \sin 2\theta \cdot \dot{\theta}.$$

Now, approximately,

$$r = \frac{h^2}{\mu}\frac{1}{1 + e\cos(\theta - \omega)} \tag{1.6}$$

where $h$ and $\omega$ are constants, and $e$ is eccentricity of orbit.

$$\therefore \frac{d}{dt}(r^2\dot{\theta})^2 = \frac{h^2\beta^2 \sin 2\theta}{1 + e\cos(\theta - \omega)}\frac{d\theta}{dt}$$

whence, on integration,

$$\dot{\theta} = \frac{d\theta}{dt} = \frac{h}{r^2}\left(\int \frac{\beta^2 \sin 2\theta\, d\theta}{1 + e\cos(\theta - \omega)}\right)^{\frac{1}{2}} = \frac{h}{r^2} I^{\frac{1}{2}}, \text{ say.} \tag{1.7}$$

Hence the operator

$$\frac{d}{dt} = \frac{d\theta}{dt}\frac{d}{d\theta} = \frac{h}{r^2} I^{\frac{1}{2}} \frac{d}{d\theta}.$$

$$\therefore \frac{d^2r}{dt^2} = \frac{h^2 I^{\frac{1}{2}}}{r^2}\frac{d}{d\theta}\left(\frac{I^{\frac{1}{2}}}{r^2}\frac{dr}{d\theta}\right) = \frac{h^2 I^{\frac{1}{2}}}{r^2}\left[\frac{I^{\frac{1}{2}}}{r^2}\frac{d^2r}{d\theta^2} + \frac{1}{2rI^{\frac{1}{2}}}\frac{dI}{d\theta}\frac{dr}{d\theta} - \frac{2I^{\frac{1}{2}}}{r^3}\left(\frac{dr}{d\theta}\right)^2\right].$$

Substituting right side of this equation in (1.5) we get, after rearranging,

$$\frac{d^2r}{d\theta^2} + \frac{1}{2I}\frac{dI}{d\theta}\frac{dr}{d\theta} - \frac{2}{r}\left(\frac{dr}{d\theta}\right)^2 - r = -\frac{\mu r^2}{h^2 I}\left(1 + \frac{\beta^2}{2}\sin^2\theta\right).$$

Changing the dependent variable in this equation by setting $u = \frac{1}{r}$, so that $\frac{dr}{d\theta} = -\frac{1}{u^2}\frac{du}{d\theta}$ and $\frac{d^2r}{d\theta^2} = -\frac{1}{u^2}\frac{d^2u}{d\theta^2} + \frac{2}{u^3}\left(\frac{du}{d\theta}\right)^2$,

we obtain, on reduction,

$$\frac{d^2u}{d\theta^2} + u = \frac{\mu}{h^2 I}\left(1 + \frac{\beta^2}{2}\sin^2\theta - \frac{h^2}{2\mu}\frac{dI}{d\theta}\frac{du}{d\theta}\right).$$

By (1.7)

$$\frac{dI}{d\theta} = \frac{\beta^2 \sin 2\theta}{1 + e\cos(\theta - \omega)} \text{ and by (1.6) } \frac{du}{d\theta} = -\frac{\mu}{h^2} e \sin(\theta - \omega),$$

to a sufficient approximation. Hence the differential equation becomes

$$\frac{d^2u}{d\theta^2} + u = \frac{\mu}{h^2 I}\left[1 + \frac{\beta^2}{2}\sin^2\theta + \frac{\beta^2}{2} e \frac{\sin 2\theta \sin(\theta - \omega)}{1 + e\cos(\theta - \omega)}\right]. \quad (1.8)$$

When it is recalled that for an undisturbed Newtonian orbit, $r^2\dot{\theta} = h$, it is evident from (1.7) that

$$I = 1 + \int_0^\theta \frac{\beta^2 \sin 2\theta\, d\theta}{1 + e\cos(\theta - \omega)}.$$

Hence (1.8) may be written

$$\frac{d^2u}{d\theta^2} + u = \frac{\mu}{h}\left[1 + \frac{\beta^2}{2}\sin^2\theta + \frac{\beta^2 e}{2}\frac{\sin 2\theta \sin(\theta - \omega)}{1 + e\cos(\theta - \omega)} - \beta^2 \int_0^\theta \frac{\sin 2\theta\, d\theta}{1 + e\cos(\theta - \omega)}\right]. \quad (1.9)$$

Solution of an equation of this form, i.e.,

$$\frac{d^2\mu}{d\theta^2} + u = f(\theta)$$

is

$$u = A\cos\theta + B\sin\theta + \int^\theta f(\xi)\sin(\theta - \xi)d\xi. \quad (1.10)$$

In expanded form, $f(\theta)$ evidently consists solely of terms in $\sin^n\theta\cos^m\theta$ so that solution will be derived from terms

$$\int^\theta \sin^n\xi \cos^m\xi \sin(\theta - \xi)d\xi = \sin\theta \int^\theta \sin^n\xi \cos^{m+1}\xi d\xi - \cos\theta \int^\theta \sin^{n+1}\xi \cos^m\xi d\xi.$$

Such integrals yield purely periodic terms (which contribute no observable effects) unless one of the exponents $n$ or $m$ is even while the other is odd. Furthermore, terms containing powers of the eccentricity $e$ above the second are negligibly small. Thus the significant terms on the right side of (1.9) are

$$\frac{\beta^2 e}{2} \sin 2\theta \sin (\theta - \omega) + \beta^2 e \int_0^\theta \sin 2\theta \cos (\theta - \omega) d\theta = f(\theta).$$

Using this result in (1.10) and discarding the small periodic terms as they appear, we get as equation of orbit,

$$u = \frac{\mu}{h^2}\left[1 + e \cos (\theta - \omega) - \frac{\beta^2 e\theta}{8} \sin (\theta - \omega)\right]$$

$$= \frac{\mu}{h^2}\left[1 + e \cos (\theta - \omega) - \frac{\beta^2 e}{8} \cos 2\omega . \theta \sin (\theta - \omega) - \frac{\beta^2 e}{8} \sin 2\omega . \theta \cos (\theta - \omega)\right]$$

which may be written with sufficient approximation

$$u = \frac{\mu}{h^2}\left[1 + \left(e - \frac{\beta^2 e}{8} \sin 2\omega . \theta\right) \cos \left(\theta - \omega + \frac{\beta^2}{8} \cos 2\omega . \theta\right)\right].$$

Hence the perihelion apse advances at rate

$$\delta\omega_0 = -\frac{2\pi}{8} \beta^2 \cos 2\omega$$

per revolution, while eccentricity increases by $\delta e_0 = -\frac{2\pi}{8} \beta^2 e \sin 2\omega$ per revolution. Evidently $\delta e_0 = \tan 2\omega . e\delta\omega_0$. Hence, using values in table[4] on right below for Mercury, $\tan 2\omega = -\frac{8.8}{8.48} = -0.104$.

$\therefore 2\omega = -6°$ or $+174°$. Since $\delta\omega$ is positive, $\cos 2\omega$ must be negative; $\therefore 2\omega = 174°$. The advance per century $\delta\omega = -\frac{2\pi}{8} \beta^2 \cos 2\omega \times \frac{100}{T}$ (where $T$ is period of revolution expressed in years), or $e\delta\omega = -\frac{25\pi e \beta^2 \cos 2\omega}{T}$. Hence for Mercury, for which $e = 0.206$ and $T = 0.24$,

$$\beta^2 = -\frac{8.48 \times 0.24 \times 5 \times 10^{-6}}{25\pi \times 0.206 \times \cos 174°} = 63.5 + 10^{-8}.$$

$\therefore \beta = 7.97 \times 10^{-4}$ and if we assume the velocity of gravitation to equal that of light, the velocity of system is $v = \beta c = 7.97 \times 10^{-4} \times 3 \times 10^{+5} = 239$ km. per sec. This is by no means unreasonably large.

Computing $e\delta\omega$ and $\delta e$ for the other inner planets on basis of above values for Mercury and table of longitudes of perihelion, and subtracting results from outstanding pre-relativity values of discrepancies we find as remaining discrepancies from observations per century:

| | PRESENT THEORY | | NEWTONIAN THEORY | |
|---|---|---|---|---|
| | $e\delta\omega$ | $\delta e$ | $e\delta\omega$ | $\delta e$ |
| Mercury | $0.00 \pm 0.43$ | $0.00 \pm 0.50$ | $8.48 \pm 0.43$ | $-0.88 \pm 0.50$ |
| Venus | $-0.05 \pm 0.25$ | $0.09 \pm 0.31$ | $-0.05 \pm 0.25$ | $+0.21 \pm 0.31$ |
| Earth | $-0.03 \pm 0.13$ | $-0.10 \pm 0.10$ | $0.10 \pm 0.13$ | $0.02 \pm 0.10$ |
| Mars | $-1.18 \pm 0.34$ | $0.05 \pm 0.27$ | $0.75 \pm 0.34$ | $0.29 \pm 0.27$ |

Thus the present theory is in good agreement with observation, the discrepancy in perihelial motion of Mars being the only one greater than the probable error. Possibly the application of this theory to the perturbation of Mars by massive Jupiter would remove the latter discrepancy.

*Case II.*—Mass of planet variable.

Here it is assumed that the inertial mass of the planet is dependent on direction of acceleration in same way as in the case of the Lorentz electron, i.e., the mass for acceleration in direction of motion is $\frac{m_0}{(1-\beta^2)^{3/2}}$ while for acceleration in perpendicular direction it is $\frac{m_0}{(1-\beta^2)^{1/2}}$ where $\beta$ is ratio of absolute velocity of planet in orbital plane to velocity of gravitation; the gravitational force depends only on the constant $m_0$. The treatment is a little less simple in this case, since the usual form of Lagrange's equations is not applicable.

If rectangular axes are chosen with sun at origin, abscissa in direction of projection of absolute constant velocity $v_0$ of sun, and $xy$-plane in plane of orbit, and if $\theta$, $\varphi$, $\omega$ and $\xi$ are angles from $x$-axis to radius vector to planet, direction of force, direction of perihelial apse and direction of instantaneous absolute motion of planet, respectively, then

$$m_0\alpha_\xi = f_\xi(1-\beta^2)^{3/2} \quad \text{and} \quad m_0\alpha_n = f_n\,(1-\beta^2)^{1/2},$$

where $\alpha$ and $f$ refer to acceleration and gravitational force, and subscripts to directions $\xi$ and perpendicular to $\xi$.

$$\therefore \quad m_0\alpha_x = m_0\left[\alpha_\xi \cos\xi + \alpha_n \cos\left(\xi + \frac{\pi}{2}\right)\right].$$

Also $$f_\xi = f\cos(\xi - \varphi) \quad \text{and}$$
$$f_n = -f\sin(\xi - \varphi).$$

Hence

$$m_0\alpha_x = f[(1-\beta^2)^{3/2}\cos\xi\cos(\xi-\varphi) + (1-\beta^2)^{1/2}\sin\xi\sin(\xi-\varphi)]$$
$$= f\left\{\left(1-\frac{\beta^2}{2}\right)[\cos\xi\cos(\xi-\varphi) + \sin\xi\sin(\xi-\varphi)] - \beta^2\cos\xi\cos(\xi-\varphi)\right\}$$
$$= f\left[\left(1-\frac{\beta^2}{2}\right)\cos\varphi - \beta^2\cos\xi\cos(\xi-\varphi)\right].$$

Similarly,

$$m_0\alpha_y = f\left[\left(1-\frac{\beta^2}{2}\right)\sin\varphi - \beta^2\sin\xi\cos(\xi-\varphi)\right],$$
$$\therefore\ m_0\alpha = m_0(\alpha_x^2+\alpha_y^2)^{1/2} = f\left[1-\frac{\beta^2}{2}(1+2\cos^2(\xi-\varphi))\right].$$

Also

$$\cot\overset{\wedge}{x\alpha} = \frac{\alpha_x}{\alpha_y} = \frac{\cos\varphi(1-\frac{1}{2}\beta^2) - \beta^2\cos\xi\cos(\xi-\varphi)}{\sin\varphi(1-\frac{1}{2}\beta^2) - \beta^2\sin\xi\cos(\xi-\varphi)}$$
$$= \cot\varphi + \beta^2\frac{\cos(\xi-\varphi)}{\sin\varphi}(\sin\xi\cot\varphi - \cos\xi).$$

Since directions of force and acceleration are but little different, we have approximately on expansion of $\cot\overset{\wedge}{x\alpha}$ in Taylor's series

$$\cot\overset{\wedge}{x\alpha} = \cot\varphi + (\overset{\wedge}{x\alpha} - \varphi)\frac{d}{d\varphi}\cot\varphi + \ldots$$
$$= \cot\varphi - (\overset{\wedge}{x\alpha} - \varphi)\csc^2\varphi + \ldots$$

Comparing the last two equations we find for angle from force to acceleration vector

$$\overset{\wedge}{x\alpha} - \varphi = -\frac{\beta^2\cos(\xi-\varphi)}{\sin\varphi\csc^2\varphi}(\sin\xi\cot\varphi - \cos\xi)$$
$$= -\frac{\beta^2}{2}\sin 2(\xi-\varphi) = -\frac{\beta^2}{2}\sin 2(\xi-\theta), \text{ approximately.}$$

Also it follows from (1.2) and (1.3) that angle from force vector to radius vector is

$$\theta - \varphi = \frac{\beta_0^2}{2} \sin 2\theta$$

where $\beta_0 = \frac{v_0}{c}$. Hence angle from radius vector to acceleration vector is

$$\nu = \overset{\wedge}{x\alpha} - \theta = (x\alpha - \varphi) - (\theta - \varphi) = \frac{\beta^2}{2} \sin 2(\theta - \xi) - \frac{\beta_0^2}{2} \sin 2\theta. \quad (2.1)$$

Now since corrections to orbit are very small we can of course compute $\beta$ from velocity in a truly elliptic orbit. By an elementary theorem the orbital velocity may then be resolved into a constant component $ev_1$ inclined at constant angle $\omega + \frac{\pi}{2}$ with $x$-axis and another constant component $v_1$ perpendicular to radius vector, i.e., inclined at angle $\theta + \frac{\pi}{2}$ with $x$-axis. Hence the orbital component of absolute velocity $v_1'$ of planet has components

$$v_x' = v_0 + ev_1 \cos\left(\omega + \frac{\pi}{2}\right) + v_1 \cos\left(\theta + \frac{\pi}{2}\right)$$

$$= v_0 - ev_1 \sin\omega - v_1 \sin\theta \text{ and}$$

$$v_y' = ev_1 \cos\omega + v_1 \cos\theta.$$

$$\therefore \beta^2 = \frac{v'^2}{c^2} = \frac{v_x'^2 + v_y'^2}{c^2}$$

$$= \beta_0^2 + \frac{1}{c^2}\{[v_1^2(1 + e^2) - 2ev_1v_0 \sin\omega] + 2ev_1^2 \cos(\theta - \omega) - 2v_1v_0 \sin\theta\}. \quad (2.2)$$

(2.1) may be written

$$\nu = \frac{\beta^2}{2}[\sin 2\theta(1 - 2\sin^2\xi) - 2\cos 2\theta \sin\xi \cos\xi] - \frac{\beta_0^2}{2} \sin 2\theta. \quad (2.3)$$

Now

$$\sin\xi = \frac{v_y'}{v'} = \frac{v_1'}{c\beta}(\cos\theta + e\cos\omega)$$

and

$$\cos\theta = \frac{v_x'}{v'} = \frac{v_0}{c\beta}\left[1 - \frac{v_1}{v_0}(\sin\theta + e\sin\omega)\right].$$

Substituting these values in (2.3), and then for $\beta^2$ from (2.2) we obtain after a few transformations

$$\nu = -\frac{v_1 v_0}{c^2}\left[\cos\theta + e\cos(2\theta - \omega)\right] - \frac{v_1^2}{c^2}\left[e\sin(\theta - \omega) + \frac{e^2}{2}\sin 2(\theta - \omega)\right] \quad (2.4)$$

If component of acceleration perpendicular to radius in direction of motion is $\alpha_\theta$, we have

$$\alpha_\theta = \alpha\cos\left(\frac{\pi}{2} + \nu\right) = -\alpha\sin\nu = -\alpha\nu = -\frac{f}{m_0}\nu = -\frac{\mu}{r^2}\nu \quad (2.5)$$

to usual approximation.

Similarly the acceleration along radius is

$$\alpha_r = \alpha\cos\nu = -\frac{\mu}{r^2}\left\{1 - \frac{\beta^2}{2}\left[1 + 2\cos^2(\theta - \xi)\right]\right\}\left(1 - \frac{\nu^2}{2}\right).$$

$\nu^2$ is negligible. Expanding $\cos^2(\theta - \xi)$ and substituting above values of $\sin\xi$, $\cos\xi$ and $\beta^2$ and dropping small constant terms and terms in $\sin^m\theta\cos^n\theta$ for which both $m$ and $n$ are even or odd, we find

$$\alpha_r = -\frac{\mu}{r^2}\left[1 + \frac{v_1 v_0}{c^2}\sin\theta - \frac{v_1^2}{c^2}e\cos(\theta - \omega)\right]. \quad (2.6)$$

In general, the components of acceleration along and perpendicular to radius vector are, respectively, $\ddot{r} - r\dot{\theta}^2$ and $r\ddot{\theta} + 2\dot{r}\dot{\theta}$. Equating these values to (2.6) and (2.5),

$$\ddot{r} - r\dot{\theta}^2 = -\frac{\mu}{r^2}\left[1 + \frac{v_1 v_0}{c^2}\sin\theta - \frac{v_1^2}{c^2}e\cos(\theta - \omega)\right]$$

and

$$\dot{r}\ddot{\theta} + 2r\dot{\theta} = -\frac{\mu}{r^2}\nu.$$

Treating these equations just as the corresponding ones in Case I were treated, we obtain the differential equation

$$\frac{d^2u}{d\theta^2} + u = \frac{\mu}{h^2 I}\left[1 + \frac{v_1 v_0}{c^2}\sin\theta - \frac{v_1^2}{c^2}e\cos(\theta - \omega) - \frac{h^2}{2\mu}\frac{dI}{d\theta}\frac{du}{d\theta}\right],$$

where

$$I = \int^{\theta} \frac{-\nu d\theta}{1 + e\cos(\theta - \omega)} = 1 - \int_{0}^{\theta} \frac{\nu d\theta}{1 + e\cos(\theta - \omega)}$$

Hence finally, if terms containing third and higher powers of $e$ are dropped,

$$\frac{d^2\mu}{d\theta^2} + u = \frac{\mu}{h^2}\left[1 + \frac{v_1 v_0}{c^2}\sin\theta - \frac{v_1^2}{c^2}e\cos(\theta - \omega) - \frac{e}{2}\frac{\nu\sin(\theta - \omega)}{1 + e\cos(\theta - \omega)} + \int_{0}^{\theta} \frac{\nu d\theta}{1 + e\cos(\theta - \omega)}\right.$$

Solving this equation by method used with Case I, we obtain

$$u = \frac{\mu}{h^2}\left\{1 + e\cos(\theta - \omega) + \frac{5}{16}e^2\frac{v_1 v_0}{c^2}\cos\omega.\theta\cos(\theta - \omega) + \frac{1}{16}e^2\frac{v_1 v_0}{c^2}\sin\omega.\theta\sin(\theta - \omega) + \frac{e}{2}\frac{v_1 v_0}{c^2}\cos\omega.\theta\right\}$$

$$= \frac{\mu}{h^2}\left\{1 + \left(e + \frac{5}{16}e^2\frac{v_1 v_0}{c^2}\cos\omega.\theta\right)\cos\left(\theta - \omega - \frac{1}{16}e\frac{v_1 v_0}{c^2}\sin\omega.\theta\right) + \frac{e}{2}\frac{v_1 v_0}{c^2}\cos\omega.\theta\right\}$$

to approximation previously used.

Thus the orbits will undergo changes of eccentricity and perihelial phase per revolution of $2\pi.\frac{5}{16}e^2\frac{v_1 v_0}{c^2}\cos\omega$ and $+2\pi.\frac{1}{16}e\frac{v_1 v_0}{c^2}\sin\omega$, respectively, together with a slow variation in radius. If $\omega$ is computed from the observed motion of Mercury, it is found that the elements for other planets are nearly zero; the agreement with observation is therefore good. The rate of variation of radius even for Mercury is small, somewhat below the limit of observation. However, the value of velocity of solar system in its own plane turns out so large (about 18,000 km. per sec.) that it would surely have shown itself in discrepancies in the times of transit of Jupiter's moons; the value of $v_0$ computed in Case I is just too small to be observable in this way.

In view of the requirement of covariance set forth by Bateman and Einstein, a theory of the kind developed in this paper can scarcely be given great weight; nevertheless it does seem to show that the classical potential theory is capable of accounting for planetary motion about as accurately as does the relativity theory, if less probably.

* Guggenheim Fellow in Physics.

[1] *Phil. Mag.*, **34** and **35**.

[2] *L'Éclairage électrique*, **16**, (1898).

[3] *Arch. Néerl.*, (2) **5**, (1900).

[4] Jeffreys, *Monthly Notices of Royal Ast. Soc.*, Dec., 1916.

# ON THE VIBRATIONAL SELECTION PRINCIPLES IN THE RAMAN EFFECT

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Various writers[1,2,3] have noted that the displacements of energy levels involved in the Raman effect should be those obtainable by superposition of two "allowed" spectral transitions. In other words, $\nu(ac)$ is a possible Raman shift if we can write $\nu(ac) = \nu(ab) + \nu(bc)$, where $\nu(ab)$, $\nu(bc)$ are possible emission or absorption frequencies. The reason for this is that the theoretical expression for a Raman line of frequency, $\nu_0 + \nu(ac)$, excited by incident light of frequency $\nu_0$ is proportional to

$$(\nu_0 + \nu(ac))^4\{|X^{(R)}_{(ac)}|^2 + |Y^{(R)}_{(ac)}|^2 + |Z^{(R)}_{(ac)}|^2\}, \qquad (1)$$

where

$$P^{(R)}_{(ac)} = \frac{E}{2h}\sum_b\left[\frac{P(ab)Z(bc)}{\nu_0 + \nu(bc)} - \frac{Z(ab)P(bc)}{\nu_0 + \nu(ab)}\right]e^{2\pi i[\nu_0 + \nu(ac)]t}. \qquad (2)$$

Eqs. (1, 2) are the same as those recently given by Hill and Kemble,[3] and embody the results of the Kramers dispersion theory. Here $X(ab)$.. denote the matrix elements of the Cartesian components of the electrical moment of the molecule in the unperturbed state, while $X^{(R)}(ab)$.... denote the perturbed or "Raman" values of these elements under excitation by plane polarized incident radiation having its electric vector $E \cos 2\pi\nu_0 t$ along the $z$ direction. Eq. (2) involves the amplitudes connected with transitions to what we shall term the "intermediate" states $b$ rather than the amplitudes $P(ac)$ of direct transition from $a$ to $c$, thus substantiating the remarks made at the beginning of the paragraph.

*Notation, etc.*—Before even stating the particular problem connected with Eqs. (1, 2) which we aim to discuss, it is perhaps well to introduce some nomenclature and qualifying remarks. We shall suppose except in the final paragraphs that the molecule is diatomic, and shall ignore the rotational fine structure. The letters $v$ and $n$ will denote, respectively, the vibrational quantum number and the totality of electronic quantum numbers. To separate the vibrational and electronic effects, it is often convenient to use a double index $n$, $v$ for the matrix arguments instead of a single index such as $a$, $b$, $c$ in Eq. (2). The term "level" is to be understood to comprise all the vibrational states having a given set of electronic quantum numbers, and we shall use the term "state" for the individual vibrational members of a level. The normal level will be denoted by $n_0$. Two levels $a$, $b$ will be said to "combine" if the unperturbed amplitude $P(ab)$ does not vanish; i.e., if $\nu(ab)$ is a possible absorption (or emission)

frequency, but not necessarily a possible Raman shift. We shall use the term "changes" in discussing the alterations of quantum numbers in ordinary absorption or emission transitions, and shall reserve the word "displacements" for the total alterations in quantum numbers between the initial and final Raman states. It is to be clearly understood that the term "intermediate" relates merely to the position of a state such as $b$ in the products in Eq. (2), and does not at all imply that its energy is intermediate between those of the initial and final Raman states, as this is usually not the case.

*Problem of the Small Raman Displacements in the Vibrational Quantum Number.*—The most commonly studied Raman lines represent displacements in the vibrational, but not in the electronic quantum numbers. However, the important intermediate states involved therein probably belong to *excited* electronic levels, as the absolute intensities of pure vibration spectra are low and hence the amplitudes connected with transitions to intermediate vibrational states belonging to the normal level are small.[4] Thus Raman displacements corresponding to infra-red vibrational frequencies are due in a certain sense to excitation of electronic absorption lines usually in the ultra-violet. The incident light is ordinarily in the visible region, and so could not excite these lines with close resonance, but nevertheless does react somewhat with the amplitudes of ultra-violet absorption, affording an illustration of what has sometimes been termed "weak quantization," especially in the old quantum theory. Now when there are electron jumps, the selection principles for the vibrational quantum number are quite different from what they are in pure vibration spectra. Whereas we can only have $\Delta v = \pm 1$ in simple harmonic, pure vibration motions, there can be enormous changes in $v$ if there are simultaneous changes in $n$. In the latter event cases are known in which $v$ changes by 20 units or so.[5] Now if a Raman displacement is expressible as the result of two consecutive jumps, one might at first thought expect Raman displacements of say 20 + 20 or 40 in the vibrational quantum number (taking this rather extreme example for concreteness).

More precisely, the allowed changes in $v$ are determined by the requirement that the initial and final states are to have the same inter-nuclear distances during appreciable time fractions of their respective motions. This is the rule advanced semi-empirically by Franck[6] and justified quantum-mechanically by Condon. Now the nuclei move slowest and spend relatively the greatest time at the extremes $r_{min}$, $r_{max}$ of their vibrational paths for a given state. Hence two states combine intensely if they have a common extremum of the inter-nuclear distance $r$. This extremum can, however, be a maximum for one state and a minimum for the other. In particular, if we start with a given vibrational state $v$ of a given electronic level $n$, changes are particularly favored to two vibrational states of another electronic level $n'$ (viz. the pair $r'_{min} = r_{min}$ $r'_{max} = r_{max}$ if $r_{min} < r'_0 < r_{max}$; the pair $r'_{max} = r_{min}$, $r'_{max} = r_{max}$ if $r'_0 < r_{min}$ the pair $r'_{min} = r_{min}$, $r'_{min} = r_{max}$, if $r'_0 > r_{max}$; here $r'_0$ denotes the equilibrium value of $r$ in the

state $n'$). This, as Condon shows, is in good agreement with experiment. If one plots initial and final vibrational quantum numbers as abscissa and ordinates, the intense changes form a "Condon" parabola, and the ordinate or abscissa representing a given state intersects this parabola twice, giving the two favored transitions from this state. To apply these ideas to the Raman effect let us start in Eq. (2) with a given initial level $a = n_0, v_0$ belonging to the normal electronic level. Let us further consider the effect of all the intermediate vibrational states belonging to a given electronic level $n$. In view of the foregoing there will be two of these states, say $n, v_1$ and $n, v_2$ which combine particularly with $n_0, v_0$. If the Raman displacement is purely vibrational, the final state $c$ belongs to the normal level $n_0$. But the intermediate state $n, v_1$ can combine with another vibrational state, say $n_0, v_3$, of the normal level besides $n_0, v_0$, as there are two favored transitions. Similarly $n_0, v_2$ can combine with another state $n_0, v_4$ besides $n_0, v_0$. As a Raman displacement is compounded from two ordinary changes, one might expect intense Raman lines corresponding to displacements $v_0 - v_3$ and $v_0 - v_4$ in the vibrational quantum number, besides of course the Rayleigh scattering $\Delta v = 0$. Such displacements represent passage from one side to the other of the Condon parabola for the intermediate level. When finally one includes all the different intermediate electronic levels in (2) one would obtain an enormous range of possible displacements in $v$, of large amounts if the important intermediate levels have widely different moments of inertia from the level $n_0$.

These hasty conclusions are not in agreement with experiment. Actually the intense Raman lines, at least in gases, involve shifts in frequency equal to the fundamental line of a pure vibration spectrum, or perhaps in some cases the first harmonic. This means that the common Raman displacements in the vibrational quantum number are only one unit, or possibly sometimes two units. The flaw in the foregoing argument predicting large displacements is the following. One must remember that according to the Condon-Franck principle, a given state combines, though with greatly varying intensity, with all the vibrational states belonging to another electronic level. In particular, we assumed in the preceding fine print that a given state combined practically entirely with only a pair of states of another level, instead of with all other vibrational states of this other level, though with reduced intensity. The reduction in intensity is, as a matter of fact, not large for states which are immediate neighbors of either of the states (the favored pair) that combine most strongly with the given initial state; this is especially true if the vibrational quantum numbers are large. In forming the sum in (2), one must therefore include the contribution of every vibrational state belonging to a given intermediate level. Furthermore, in adding these contributions, one must be very careful to consider the *phases* of the matrix elements involved therein. One finds that the phase effects give reinforcement when the initial and final levels $a$ and $c$ are the same, the case of Rayleigh scattering. (At least this is true for the $z$ component, as $\measuredangle(ab)\measuredangle(ba) = |\measuredangle(ab)|^2 > 0$ and so all the terms to be added have the same sign, as with a given intermediate level the variation in the denominator from term to term in the summation in (2) is negligible.) On the other hand, because of the di-

versity of phase factors for the different intermediate states belonging to a given electronic level, one suspects that the various terms in the summation will largely annul each other if the initial and final states $a$ and $c$ differ widely in their value of $v$. If, however, the states $a$ and $c$ are adjacent, i.e., if the Raman displacement in $v$ is only one unit, the annulment might be very incomplete, as this case is very close to that of reinforcement. By a somewhat similar qualitative reasoning, Hill and Kemble[3] briefly stated that the phase relations explain why there are only small Raman displacements in the vibrational quantum number. The purpose of the present paper is to give a more quantitative and rigorous proof of this proposition of the usual absence of all displacements except the fundamental $\Delta v = \pm 1$. The writer is informed that C. Manneback is also publishing a proof, but by a method somewhat different from ours, so that the present note is perhaps not superfluous.[7]

*Mathematical Preliminaries.*—We shall first develop a multiplication scheme for what we shall call "hybrid matrix elements," whose use is the essence of the proof. Let $\Psi_v$ and $\Phi_v$ ($v = 0, 1, \ldots$) be two *different* sets of orthogonal normalized functions of a variable $r$, so that

$$\int \Psi_v^* \Psi_{v'}\, dr = \delta_{v'}^v, \qquad \int \Phi_v^* \Phi_{v'}\, dr = \delta_{v'}^v, \tag{3}$$

with the asterisk denoting the complex conjugate. For example, and more especially for our purposes, $\Psi_v$ and $\Phi_v$ might be the vibrational wave functions for two different electronic levels. Let $f(r)$ be any function of $r$, and also if desired of the operator $\partial/\partial r$. Expand $f(r)\Psi_v$ as a series in the $\Phi_v$, thus

$$f(r)\Psi_v = \sum_{v'} f_{\Phi\Psi}(v';\ v)\Phi_{v'}. \tag{4}$$

The coefficients in this expansion we shall term the hybrid matrix elements of $f$, as they differ from ordinary matrix elements in that the wave function on the left belongs to a different set of orthogonal functions from those on the right. The ordinary elements correspond to the special case $\Psi = \Phi$. On multiplication of (4) by $\Phi_{v''}$ and integration throughout the domain of $r$, we see, using (3), that

$$f_{\Phi\Psi}(v'';\ v) = \int \Phi_{v''}^* f \Psi_v dr. \tag{5}$$

Let $\Theta_v(r)$ be still a third set of normalized orthogonal functions. The important property of the hybrid elements is that they obey the following law of multiplication

$$(fg)_{\Theta\Psi}(v'';\ v) = \sum_{v'} f_{\Theta\Phi}(v'';\ v') g_{\Phi\Psi}(v';\ v). \tag{6}$$

To prove (6), note that $fg\Psi_v(r)$ can be expressed equally well as

$$\sum_{v''} (fg)_{\Theta\Psi}(v'';\ v)\Theta_{v''}(r), \tag{7}$$

or as

$$f\sum_{v'} g_{\Phi\Psi}\,\Phi(v';\,v) \;=\; \sum_{v',\,v''} f_{\Theta\Phi}(v'';\,v')g_{\Phi\Psi}(v';\,v)\Theta_{v''}(r). \qquad (8)$$

The result (6) follows immediately on comparing coefficients in (7) and (8). Besides the above multiplication law, the hybrid matrix elements obviously obey the ordinary elementary addition law. Incidentally, these elements for $f = 1$ are not the ordinary Christoffel symbols $\delta_v^{v'}$ since $\Psi$ and $\Phi$ are not orthogonal, but do have the property that

$$\sum_{v'} 1_{\Theta\Phi}(v'';\,v')1_{\Phi\Psi}(v';\,v) \;=\; \delta_v^{v''}.$$

As we have agreed to disregard the rotational factor, the total wave function of the molecule is approximately the product of an electronic wave function $U(x_1, \ldots z_f, r)$ and a vibrational one $R(r)$. Here $R$ is a function only of the inter-nuclear distance $r$, while $U$ is a function of the Cartesian coördinates of the electrons, measured in a system of reference fixed relative to the nuclei, and also involves $r$ as a parameter. As the electronic and nuclear variables are not rigorously separable in the Schroedinger equation, this resolution of the wave function into electronic and vibrational factors is not exact, but is a good approximation if the vibrational distortion is not too large. It permits us to resolve the total energy $W_{nv}$ into electronic and vibrational parts, so that

$$W_{nv} \;=\; W(n) + W_n(v), \qquad (9)$$

where $W(n)$ is the energy for a system in which the nuclei are at rest at the equilibrium distance appropriate to the state $n$, and $W_n(v)$ is the vibrational energy measured relative to an origin at this equilibrium position. By the Schroedinger-Eckart rule, the elements of any function $f$ are given by[8]

$$f(n'v';\,nv) \;=\; \int \ldots \int\int U^*_{n'}\, R^*_{n'v'} f\, U_n\, R_{nv}\, dx_1 \ldots dz_f\, dr. \qquad (10)$$

If we omit the vibrational wave factors and integrate over the electronic coördinates, we thereby define a function of $r$

$$f_{n'n}(r) \;=\; \int \ldots \int U^*_{n'} f\, U_n\, dx_1 \ldots dz_f, \qquad (11)$$

which of course involves the initial and final electronic quantum numbers $n'$, $n$ as parameters. We shall write in the electronic quantum numbers as subscripts whenever they appear as parameters in the vibrational problem. Eqs. (5, 10, 11) show that a complete matrix element is a hybrid matrix element in which $f_{n'n}(r)$, $R_{n'v}$, $R_{nv}$ now play the same roles as $f(r)$,$\Phi_v$, $\Psi_v$ in the notation used in connection with Eqs. (3–5). The rule (6) shows that

$$(f_{n''n'}\, g_{n'n})(v'';\,v) \;=\; \sum_{v'} \; f_{n''n'}\,(v'';\,v')g_{n'n}(v';\,v), \qquad (12)$$

which is not to be confused with the ordinary law of complete matrix multiplication in which the summation over the intermediate states is with respect to both $n$ and $v$, and so includes all possible electronic levels, whereas in (12) it includes only the vibrational states of one particular electronic level. It is to be understood that for this reason an element $(v'', v)$ of $f_{n''n'}\, g_{n'n}$ is not the same as the corresponding element of $(fg)_{n''n}$.

*Proof That Only Small Raman Displacements in the Vibrational Quantum Number Are Possible.*—After the mathematical preliminaries, this proof is quite simple. In view of (9) and the significance of the states $a$, $b$, $c$ in the more explicit notation, the Bohr frequency condition may be written as follows:

$$h\nu(ab) = W(n_0) + W_{n_0}(v_0) - W(n) - W_n(v'),$$
$$h\nu(bc) = W(n) + W_n(v') - W(n_0) - W_{n_0}(v''). \qquad (13)$$

Let us substitute (13) in (2), and for simplicity sum until further notice over only the intermediate states belonging to one particular electronic level. As the vibrational energy is small compared to the denominators in (2), we may expand (2) as a power series in $W_n(v')$, thereby bringing $W_n(v')$ in the numerator rather than denominator. Similar expansions in $W_{n_0}(v)$ and $W_{n_0}(v'')$ prove unnecessary, as they are constant with respect to the summation. We thus find for the part of (2) resulting from the intermediate level $n$

$$\alpha \sum_{v'} \{ [A^{-1} - A^{-2} W_n(v') + A^{-3} W_n(v')^2 + \ldots] [P(n_0 v; nv') Z(nv'; n_0 v'')]$$
$$- [B^{-1} + B^{-2} W_n(v') + B^{-3} W_n(v')^2 + \ldots] Z [(n_0 v; nv') P(nv; n' v'')], \qquad (14)$$

where

$$\alpha = \tfrac{1}{2} E e^{2\pi i [\nu_0 + \nu(ac)]t}, \qquad A = h\nu_0 + W(n) - W(n_0) - W_{n_0}(v''),$$
$$B = h\nu_0 + W(n_0) + W_{n_0}(v) - W(n).$$

We have included only terms of the first and second orders in $W_n(v')$, but incorporation of higher orders would occasion no difficulty and would not affect our conclusions. Now the $W_n(v')$ are the diagonal matrix elements of the Hamiltonian function $H_{nn}$ for the vibrational problem of the state $n$, while the non-diagonal elements are zero as the energy is a diagonal matrix. Hence the first part of (14) can be written

$$\alpha \sum_{v', v^{III}} \{ P_{n_0 n}(v; v') (A^{-1} - A^{-2} H_{nn} + A^{-3} H_{nn}^2)(v'; v^{III}) Z_{nn_0}(v^{III}; v'') . \qquad (15)$$

Here we have used the notation $P_{n_0 n}(v; v')$ rather than $P(n_0 v; nv')$, etc., in order to conform to the usage in Eq. (12). We henceforth do not bother to write out the terms arising from the second part of (14), as the manipulation of these terms is similar to that of those from the first part, and can be supplied by the reader. The hybrid multiplication law (6) or (12)

when extended to a triple rather than double product, and use of formula (5) shows that (15) is the same as

$$\alpha \int R^*_{n_0 v} \{ P_{n_0 n} (A^{-1} - A^{-2} H_{nn} + A^{-3} H^2_{nn}) Z_{nn_0} \} R_{n_0 v''} \, dr. \qquad (16)$$

Here the $P_{n_0 n}$, etc., are constructed in the fashion (11) by integrating only over the electronic coördinates, and $H_{nn}$ is the operator

$$H_{nn} = \frac{1}{2M} \left( \frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + V_n(r),$$

corresponding to the vibrational problem of the state $n$. The important thing is that in (16) the summations over $v'$, $v^{III}$ have been entirely eliminated. To evaluate (16) exactly it would be necessary to know the vibrational potential energy function $V_n(r)$ for the excited or intermediate level $n$, but the vibrational wave functions $R_{nv}$ for this level are no longer required. Only those $R_{n_0 v}$, $R_{n_0 v''}$ of the normal level are needed. The dependence of the factors $P_{n_0 n}$, $Z_{nn_0}$ on $r$ is also required, and is in general not known in detail. We may, however, expand these expressions as power series in $(r - r_0)$ if the vibrational excitation in either of the states $n_0 v$ or $n_0 v''$ is small. For then either $R_{n_0 v}$ or $R_{n_0 v''}$ is vanishingly small except in the vicinity of the equilibrium value $r_0$ of the inter-nuclear distance for the state $n_0$. This condition is presumably met in the initial state $n_0 v$, as the concentration of molecules in excited vibrational states is usually negligible under ordinary conditions of temperature, etc. The expansion of (16) takes the form

$$\alpha \int R^*_{n_0 v} \{ [a + b(r - r_0) + c(r - r_0)^2 + \ldots][A^{-1} - A^{-2} H_{nn} + A^{-3} H^2_{nn}] \\ [g + h(r - r_0) + i(r - r_0)^2] \} R_{n_0 v''} \, dr. \qquad (17)$$

Since the equilibrium distance $r_n$ for the state $n$ is not the same as that $r_0$ for the state $n_0$, the expansion of the potential energy for the state $n$ will contain constant and linear terms in $r - r_0$, whereas the expansion of that for the state $n_0$ will commence with quadratic terms. Hence the expansions of the vibrational Hamiltonian functions for these two states are, respectively, of the form

$$H_{nn} = \frac{1}{2M} \left( \frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + d + e(r - r_0) + f(r - r_0)^2,$$

$$H_{n_0 n_0} = \frac{1}{2M} \left( \frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + f_0(r - r_0)^2.$$

Subtraction of these two expressions yields us a formula

$$H_{nn} = H_{n_0 n_0} + d + e(r - r_0) + (f - f_0)(r - r_0)^2 + \ldots \qquad (18)$$

for $H_{nn}$ which can be substituted in (17) and which is especially convenient because it does not involve the differential operator $(h/2\pi i)^2\partial^2 \ldots/\partial r^2$. Unless some of the coefficients $a$, $b$, etc., happen fortuitously to be particularly small, we can suppose that the terms in (17) having factors $(r - r_0)^0$, $(r - r_0)$, $(r - r_0)^2$ are of rapidly decreasing orders of magnitude, as we supposed at least one of the wave functions $R_{nov}$, $R_{nov'}$ very small except in the vicinity of $r_0$. To a sufficient approximation, the vibrational problem of the normal level may be supposed simple harmonic, making $R_{nov}$, $R_{nov'}$ Hermitian orthogonal functions. Then by the familiar selection rule for the harmonic oscillator, the matrix elements of $r - r_0$ are entirely of the form $\Delta v = \pm 1$, while those of $H_{non_0}$ are, of course, entirely of the type $\Delta v = 0$. (The elements of $H_{nn}$ would not be of this type, as they are diagonal with respect to the $R_{nv}$ rather than $R_{nov}$; for this reason the substitution of (18) in (17) is necessary.) By the Schroedinger-Eckart rule, the integral (17) is merely a matrix element of the part of the integrand inclosed in parentheses. Hence by the rules for matrix multiplication, the parts of (17) which are of orders $(r - r_0)^0$, $(r - r_0)$, $(r - r_0)^2$ vanish unless, respectively, $\Delta v = 0$, $\Delta v = \pm 1$, $\Delta v = 0$, $\pm 2$. Thus the most intense scattered lines are of the form $\Delta v = 0$, i.e., represent simple Rayleigh scattering, while the most intense Raman lines are those $\Delta v = \pm 1$ whose displacement equals the fundamental of the vibrational frequency. Less intense still are the Raman lines $\Delta v = \pm 2$, whose displacement equals the harmonic of the vibrational frequency, and which are ordinarily far too weak to detect experimentally. This is the desired result. There can be no question of large vibrational transitions, corresponding to passage from one side of the Condon parabola to the other for the intermediate level, as this idea has been dropped out of consideration by using the hybrid multiplication law. Our proof has hitherto involved the restriction of the summation in (2) to one particular intermediate electronic level, but the inclusion of all levels[9,10] merely yields a linear combination of expressions of the type form (17), and so cannot cause large Raman displacements in $v$.

*Polyatomic Molecules.*—Essentially the same considerations as in the rest of the paper can be applied to molecules composed of more than two atoms. The main difference is that instead of one vibrational coördinate $r$, we must utilize several $r_1$, $r_2$, . . . which are identical with "normal coordinates" if the vibrations are simple harmonic, and which are associated with different kinds of vibrational quantum numbers $v_1$, $v_2$, . . . The same general method as before is applicable. We find that the scattered lines should rank as follows in intensity: first, Rayleigh scattering; second, Raman lines whose displacements equal one of the fundamental vibration frequencies; third, Raman lines whose displacements are either harmonics of a fundamental vibration frequency, or else are "combination fre-

quencies" equal to the sum of two different fundamentals. However, Raman lines which are usually considered to be of the combination type have been reported experimentally without any trace of Raman shifts equal to the fundamental absorption frequencies. In other words, lines which we have ranked third in intensity are apparently found without those we ranked second. Instances in solids or liquids will not be cited, as our theory is primarily for gases. In $CO_2$ Rasetti[2] finds only Raman shifts of 1284 and 1392 ($\pm$ 10) cm.$^{-1}$ which are not equal to absorption lines, but which are expressible as difference combinations of the two components (3616 and 3720 cm.$^{-1}$) of the doublet absorption band at 2.7$\mu$ with that at 4.28$\mu$ (2336 cm.$^{-1}$). To account for this anomalous situation two different suppositions (I) or (II) might be made.

(I) One possibility is that the intense Raman lines in $CO_2$ are fundamentals, and have been misinterpreted as combinations. Eucken's[11] collinear model of the $CO_2$ molecule does indeed have a fundamental at 1174 cm.$^{-1}$, which Rasetti[12] notes is in the vicinity of his Raman lines, but it is doubtful whether all the details of Eucken's model are tenable. It is perfectly possible for a fundamental to be inactive as an absorption line, but to appear as a Raman line. This will be the case for symmetrical vibrations, which do not create an electrical moment in the molecule in the ordinary (dielectric constant) sense, but which will in general change the magnitude of the moment matrix elements associated with transitions to excited electron levels, and so cause non-vanishing coefficients $b$, $h$ in Eq. (17). In Eucken's model, for instance, the 1174 cm.$^{-1}$ vibration is inactive in absorption and corresponds to symmetrical displacements of the two O nuclei relative to the C nucleus at the center, thus merely stretching the molecule without altering its symmetry. The sole Raman displacement which Wood[13] finds in $NH_3$ vapor corresponds to an observed absorption band at 3$\mu$. The very careful recent analysis of the $NH_3$ vibration spectrum by Stinchcomb and Barker[14] shows that the 3$\mu$ vibration is due to oscillations in the altitude of the molecular pyramid, which has the N nucleus at its vertex and the H nuclei at the corners of its base. Their measurements do not reveal whether the 3$\mu$ vibration is a fundamental, but Wood's observation of a 3$\mu$ Raman displacement is strong evidence that this vibration is really a fundamental, and it is indeed so classed in Dennison's[15] model of the $NH_3$ molecule. The non-appearance of the other fundamentals as Raman lines suggests that stretching the altitude of the molecular pyramid distorts the moment matrix elements more than do the other normal modes of vibration.

(II) In the particular[16] case of $CO_2$ another possibility, for which the writer is indebted entirely to Professor Dennison, is that the Raman displacements observed by Rasetti are not pure vibration lines, but rather a combination of rotation and vibration. In a collinear model the energy

of small oscillations of the C nucleus in the median plane (the perpendicular bisector of the line segment joining the two O nuclei) is proportional to $2n_r + n_\varphi$.[17] Here $n_r$ and $n_\varphi$ are respectively the radial and azimuthal quantum numbers for motions of the C nucleus in the median plane. Hence the apparent vibrational quantum number is $2n_r + n_\varphi$. Now Kemble and Hill,[3] for instance, have shown that only Raman displacements of only 0 and 2 units are possible in rotational quantum numbers such as $n_\varphi$. Hence in the Raman effect $2n_r + n_\varphi$ can be displaced only by an even number of units. In investigations not yet published, Dennison interprets the absorption band of $CO_2$ at 673 cm.$^{-1}$ as due to a unit change in $2n_r + n_\varphi$. The Raman displacements found by Rasetti are approximately double this, and hence might be interpreted as displacements of 2 units in $2n_r + n_\varphi$. This does not contradict the preceding theory in our paper because $n_\varphi$ is a rotational rather than vibrational quantum number. It is, however, quite different from the usual rotational quantum number in that its effect on the energy is as large as that of vibrations. This is because of the anomalous collinear character of the $CO_2$ molecule, in virtue of which the moment of inertia about the axis of figure is very small, in fact, zero when the C nucleus is exactly at its equilibrium position.

[1] A. Smekal, *Naturwissenschaften*, **11**, 873 (1923); **16**, 612 (1928); H. A. Kramers and W. Heisenberg, *Zeits. Physik*, **31**, 681 (1925); M. Born, *Naturwissenschaften*, **16**, 673 (1928); A. Sommerfeld, *Atombau und Spektrallinien—Wellenmechanischer Ergänzungsband*, p. 203; R. M. Langer, *Nature*, **123**, 345 (1929); G. H. Dieke, *Ibid.*, **123**, 564 (1929).

[2] F. Rasetti, *Nature*, **123**, 205 (1929); *Proc. Nat. Acad. Sci.*, **15**, 234 and 515 (1929).

[3] E. C. Kemble and E. Hill, *Ibid.*, **15**, 387 (1929).

[4] The small effect of the pure vibration amplitudes can be demonstrated by the same type of numerical calculation as used by the writer in showing that they do not contribute appreciably to the dielectric constant. See J. H. Van Vleck, *Phys. Rev.*, **30**, 41–44 (1927).

[5] Cf., for instance, Fig. 7 in E. U. Condon, *Phys. Rev.*, **28**, 1182 (1927).

[6] J. Franck, *Trans. Faraday Soc.*, **21**, part 3 (1925); E. U. Condon, *Proc. Nat. Acad. Sci.*, **13**, 462 (1927); *Phys. Rev.*, **32**, 858 (1928).

[7] Manneback has already given a preliminary account of his results, without any of the details of the proof, *Naturwissenschaften*, **17**, 364(1929).

[8] The "weight function" $r^2$ appearing when the volume element $dv = r^2 \sin\theta\, dr\, d\theta\, d\varphi$ is expressed in polar coördinates can be eliminated by incorporation of a factor $r$ in the vibrational wave function, and so is not included in the integrand of (10).

[9] We tacitly assume that the superposition effects in adding the contributions of the various intermediate electronic levels do not essentially change the conclusions. These effects could cause destructive interference and so be of importance only if the different intermediate levels gave different signs for the coefficients $b,h$ in (17) in such a way that when expressions of the form (17) are summed over all the intermediate levels, the term of the first order in $r-r_0$ disappears. This appears highly unlikely, as probably changing the inter-nuclear distance affects most of the amplitudes in the same direction, so that most of the coefficients $b,h$, have the same sign. In any event

an exact cancellation of the first order terms would be exceedingly fortuitous (also a remotely possible explanation of the phenomena found by Rasetti in $CO_2$). Such interference effects might, however, conceivably explain why incident radiations of certain frequencies are more effective than others in exciting particular Raman lines even without any approach to resonance with the frequencies of the atom.

[10] In summing over the various intermediate electronic levels, the case $n = n_0$ in which the intermediate level is identical with the normal level requires special treatment. The first coefficients $a,g$, in (17) vanish for $n = n_0$ if the molecule is non-polar. Even with a polar molecule, it can be shown that due to cancellation of the first and second half of (2) the result for $n = n_0$ is the same as if $a,g$ were omitted entirely. The lowest non-vanishing term in the integrand then becomes of order $(r - r_0)^2$. For this reason Raman displacements $\Delta v = \pm 2$ can here, unlike the usual case of excited intermediate levels, be expected to be comparable with $\Delta v = \pm 1$. If, however, the motion is simple harmonic (but not necessarily isotropic, so that the normal coördinates need not be orthogonal) all the Raman displacements arising from intermediate terms of the form $n = n_0$ vanish, as it is readily seen that in this particular case the first and second halves of (2) cancel. This unusual behavior in the case $n = n_0$ does not affect our conclusion because we have already mentioned near the beginning of the paper that in the summation the normal intermediate states make a very small contribution compared to the excited intermediate states, at least in gases. It is conceivable, however, that the amplitudes of pure vibration become more important in solids.

[11] A. Eucken, *Zeits. Physik*, **37**, 714 (1926).

[12] F. Rasetti, *Nature*, **123**, 757 (1929); cf. also P. N. Ghosh, *Ibid.*, **124**, 92 (1929).

[13] R. W. Wood, *Phil. Mag.*, **7**, 744 (1929).

[14] G. A. Stinchcomb and E. F. Barker, *Phys. Rev.*, **33**, 305 (1929); E. G. Barker, *Ibid.*, **33**, 684 (1929).

[15] D. M. Dennison, *Phil. Mag.*, **1**, 195 (1926).

[16] A. S. Gavesan and S. Venkateswaran report results on $CS_2$ similar to those of Rasetti on $CO_2$ in that the prominent Raman lines are different from the important, presumably fundamental, absorption lines. Dielectric constant data show that $CS_2$ is non-polar, or at least nearly so, so that it may be collinear, in which case the same theory can be used for $CS_2$ as for $CO_2$. *Nature*, **124**, 57(1929).

[17] Cf. Sommerfeld, *Atombau*, 4th Ed., p. 789, Eq. (29).